İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

MICROENCAPSULATION OF COCONUT OIL / VITAMIN E AND ENHANCING THE WASHING DURABILITY OF MICROCAPSULES

Ph.D. Thesis by
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Department: Textile Engineering

Programme: Textile Engineering

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

KOKONAT YAĞI / VİTAMIN E NİN MİKROKAPSÜLASYONU VE MİKROKAPSÜLLERİN YIKAMA DAYANIMLARININ ARTIRILMASI

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TEMMUZ 2007

I would like to dedicate this thesis to my dearest wife, Arzu, for her continuous encouragement and greatest support.

FOREWORD

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SUMMARY

In this study, as active ingredient of the microcapsule, Myritol 318 (coconut oil) and vitamin E were used together. And the wall membrane of the microcapsule was formed by a kind of carboxyl-polymer. By using foulard (pad) and exhaust processes, the microcapsules that contain Myritol 318 (coconut oil) and vitamin E mixtures were applied on Supplex fabric, which is 240 g/sqm. The fiber composition of this fabric is % 90 Polyamide, % 10 Lycra by Invista. The fabric type is 30/1 single jersey. Different type of recipes was formed by using different type of binder qualities and different size of microcapsule diameters. By this way, the effect of different binder characteristics, the effect of microcapsule mean size, and the performance of the foulard (pad) and exhaust processes could have been investigated and compared to each other.

SEM image analyses and gas-chromatographic analyses of prepared recipes have been evaluated for further washings so that the most suitable recipe configuration can be found out for the usage in apparel industry.

It was found that the hydrophobic characterized binder qualities, binder 3001A and 3002A combination and also 3009A gave us much better laundering resistance due to the fact that they were much stronger binders than 3003A. Especially in binder 3003A, since this binder quality is hydrophilic characterized and is not enough strong, in further laundering cycles, it could not resist enough against water and the microcapsules attached onto fabric were released after 5^{th} laundering cycles. In exhaust process, since the liquor ratio is higher than foulard process, the microcapsule affinity onto the fabric became much difficult. That's why Nanox 1166 agent has to be used as an extra additive to increase the affinity of the microcapsules onto the fabric. Otherwise, most of the capsules might have stayed in the bath and wasted.

In this study, it was figured out that when examining the mean size of the microcapsules, microcapsules individually might behave different than when they attach to the fabric by binders. It means, it is clear that smaller size of microcapsules will individually tend to release its active ingredient quicker than the bigger capsules, because, the diffusion rate and the risk of the capsule shell breakage will be higher in small size of capsules due to its thinner membrane wall. However, when the capsules are attached to the fabric, capsules behavior may be partly different due to the fact that the environment conditions of the capsule are different than its individual statement. Binder makes this difference. Normally, smaller size of capsules diffusion rate is higher due to its bigger surface than bigger capsules in the same weight proportion. However, the coverage of the binder also helps to improve the lost index for smaller size capsules and their breaking risk gets lowered like the big size of capsules more or less. On the other hand, we also do not want to microcapsules to

totally embedded under the binders. Otherwise, their active ingredient is totally masked and could not perform anymore. So, what is needed is having the best controllable release rate.

To be able to have a better controllable release rate against any further laundering process, second coating with chitosan is made onto already microcapsule treated fabric via foulard process. To search the potential positive benefit of chitosan on laundering durability, gas-chromatographic analysis is also made on microcapsule treated fabric. “With” and “without” chitosan applied recipes are compared to each other. And a visible positive progress is achieved when chitosan coating is made onto the already microcapsule treated fabric against further laundering processes. Vitamin E and Myritol 318 Oil release from microcapsules could be taken under much better control and between 10 to 42.8% microcapsul lost could be decreased. It means, better controllable release rate have been achieved. The main reason behind of this positive result is that chitosan acted as a second wall material of the microcapsules, which were already attached to fabric by binder. Double wall means slower diffusion rate and stronger wall for the capsules used in this study.

The second main benefit of chitosan is that it has controllable pore size and density, when the temperature is increased the pores of chitosan are shrunk. This means, in the chitosan coated microcapsule treated fabric; the capsules wall will be stronger after the curing temperature at 120 °C. This will improve the laundering durability of the chitosan coated microcapsule treated fabric.

KOKONAT YAĞI / VİTAMIN E NİN MİKROKAPSÜLASYONU VE MİKROKAPSÜLLERİN YIKAMA DAYANIMLARININ ARTIRILMASI

ÖZET

Bu çalışmada mikrokapsüllerin aktif maddesi olarak myritol 318 yağı ve vitamin E karışımı birlikte kullanılmıştır. Mikrokapsüllerin dış duvarı bir çeşit karboksilik asit polimeri kullanılarak oluşturulmuştur. Emdirme (fular) ve çektirme prosesi kullanılarak, myritol 318 kokonat yağı/ vitamin E karışımlı mikrokapsüller 240g/m^2 gramajındaki Supplex kumaşa uygulanmıştır. Kumaşın lif karışımı; %90 poliamid ve %10 Lycra' (Invista) dır ve kullanılan kumaş 30/1 süpremdir. Farklı tipte binder kaliteleri ve farklı büyüklükte mikrokapsül çapları kullanılarak farkli reçeteler oluşturulmuştur. Bu yolla, farklı binder özelliklerinin, mikrokapsül çap büyüklüklerinin, fular ve çektirme proseslerinin performanslarının mukayasesini ve incelemesini yapabilmek mümkün olmuştur.

Hazırlanan reçeteler, elektron mikroskobu altinda ve gaz kromatografi analizleriyle değerlendirilerek, hazır giyim endüstrisinde kullanılabilecek en uygun reçete tipinin tespit edilebilmesi mümkün olabilmiştir.

Hidrofob karakterli 3001A-3002A binder kombinasyonu ve 3009A binderi, kuvvetli binder özelliklerinden dolayı mikrokapsülleri müteakip yıkamalara karşı koruyabildiklerinden daha iyi bir yıkama dayanımı sağlamıştır. Özellikle binder 3003A kalitesi yeteri kadar kuvvetli bir binder olmadığından dolayı, mikrokapsüller suya karşı gereği kadar dayanıklı olamamıştır ve kumaş üzerindeki mikrokapsüller 5. yıkamadan sonra büyük ölçüde serbest bırakılmışlardır. Çektirme yönteminde, flotte oranı emdirme yönteminden daha yüksek olduğu için, mikrokapsüllerin kumaşa olan afiniteleri de güçleşir. Bu yüzden Nanox 1166 adlı kimyasal mikrokapsüllerin kumaşa olan afinitesini artırmak için kullanılmıştır. Aksi takdirde, kapsüllerin birçoğu flottede kalırdı ve boşa giderdi.

Bu çalışmada, mikrokapsül büyüklükleri incelendiğinde, mikrokapsüllerin tek başlarına gösterdikleri davranış biçimiyle, binderle kumaşa bağlandıklarında gösterdikleri davranış biçimlerinin birbirinden farklılık gösterebileceği gözlemlenmiştir. Yani, küçük çaplı mikrokapsüllerin tek başlarına içerdikleri aktif maddeleri büyük çaplı mikrokapsüllerden daha hızlı verme eğiliminde olacakları aşikardır. Çünkü; salınım oranı ve kapsül duvarının kırılma riski küçük mikrokapsüllerde ince duvar kalınlıklarından dolayı daha fazladır. Öte yandan, kapsüller kumaşa bağlandıklarında, kapsüllerin davranışları dış etkilerden dolayı, tek başlarınayken gösterdikleri davranışlardan farklılık gösterebilmektedir. Bu farklılığa yol açan binderdir. Normalde, aynı ağırlık oranında, daha fazla yüzey alanına sahip olmalarından dolayı küçük kapsüllerin yok olma hızı büyük kapsüllerinkinden daha fazladır. Ama, binder kaplaması küçük kapsüllerin yok olma indeksini iyileştirebilir ve kapsüllerin kırılma riskini büyük kapsüllerdekine benzer şekilde azaltabilir. Diğer taraftan, mikrokapsüllerin tamamen de binderin altında kalması istenmez. Bu durumda, aktif madde tamamen atıl kalır ve performans gösteremez. Bu yüzden, gerçekten gerekli olan, daha iyi bir şekilde kontrol edilebilen salınım oranıdır.

Müteakip yıkamalara karşı daha kontrollü bir salınım oranına sahip olabilmek için, ikincil bir kaplayıcı olarak, halihazırda mikrokapsül uygulanmış Supplex kumaş üzerine fular prosesiyle chitosan kaplaması yapılmıştır. Chitosanın yıkama dayanımındaki olası pozitif etkisini incelemek için, gaz kromatografik analizlerler mikrokapsül uygulanmış kumaşlara yapılmıştır. Chitosan uygulanmış ve uygulanmamış reçeteler birbiriyle mukayese edilmiştir. Hali hazırda mikrokapsül tatbik edilmiş kumaş üzerine chitosan kaplaması yapıldığında yıkama dayanımı için pozitif yönde kayda değer bir ilerleme sağlanmıştır. Vitamin E ve myritol 318 yağının mikrokapsüllerden salınımı daha iyi kontrol altına alınabilmiştir ve % 10 ila % 42.8'lik oranda mikrokapsül kayıpları azaltılabilmiştir. Yani, daha kontrollu bir salınım oranı sağlanabilmiştir. Bu pozitif sonucun arkasında yatan ana sebep, chitosanın halihazırda kumaş üzerine binderle tutunmuş olan mikrokapsüller için, ikincil bir duvar materyali olarak fonksiyon göstermesidir. Çift duvarın anlamı bu tezde kullanılan kapsüllerin daha dayanıklı olması ve daha yavaş bir aktif madde salınım hızına sahip olmalarıdır.

Chitosanın ikinci faydası, kontrol altında tutulabilen delikli bir yapıya ve yoğunluğa sahip olmasından dolayı, sıcaklık arttıkça bu deliklerin büzülebilmesi ve kapanmaya başlamasıdır. Bunun anlamı mikrokapsül uygulanmış kumaşa chitosan kaplaması yapıldığında kapsül duvarının 120 °C olan fikse şartlarında daha dayanıklı hale gelmesidir. Bu da mikrokapsül tatbik edilmiş kumaşa chitosan kaplaması yapılması neticesinde yıkama dayanımının artmasıdır.

1. INTRODUCTION

Between 1988 and 1998, the share of textiles (and shoes) in private spending decreased from 7,1% to 5,1% in Europe [1]. Since the last decade, this trend has unfortunately still continued in this direction for the global textile market. Personal computers, digital cameras and mobile phones are attracting the available income, especially of western consumers, more successfully than textiles. None of proposed solutions such as shorter fashion cycles and ever-cheaper prices has been able to reverse the tendency so far. The call for a cure is hence still very loud. Somehow, textiles must be made more appealing to the modern consumer.

One key idea is making its way into many heads: garments must become more than a practical way to stay covered, warm and nice looking. They must also become more than a means of individual differentiation or group identification, which is the main purpose of fashion. Therefore, it is needed to usher a new era in textile market. This is called as “Active Textile”. End consumers have opportunities to buy more than a garment; beside that they have started to have more additional functions on the garment that they buy. These additional functions could have been value added to the garments after a long time active textile researches by many researchers in different countries.

A new national survey in US reveals that the majority of Americans are now looking for more versatile clothes that have added performance. Results from the survey commissioned by Nano-Tex, a leading provider of textile-enhancing treatments to apparel companies, show that 82 percent of Americans want more performance features- including stain, odor, wrinkle free and/or fade resistance and perspiration control- in their clothes [2].

Interestingly, men and women differ in their beliefs of which needs clothes with extra performance- stain and spill resistance, moisture control, and odor control and wrinkle resistance. Sixty-five percent of men say that men’s clothes most need extra performance, while women were virtually evenly split in thinking that men’s, kid and women’s clothes all need the extra performance. In addition, when asked about

interest in odor-control clothes, 51 percent of men say they'd buy an odor-control T-shirt for themselves, but 31 percent says they'd buy on for someone else. Women aren't quite so shy: while only 39 percent of women indicated that they would buy odor control themselves, 51 percent say they would buy one for someone else [2].

Nano-technologies are increasingly commonplace in the textile industry. This market is already worth US$11bn and is set to grow by a factor of ten by 2012. In fact, the textile industry is poised to be the first sector to experience a major impact from nano-technologies [3]. "Nan technologies for the Textile Market" calculates the market for textile making use of Nano-technologies will be worth US$13,6bn by 2007, expanding to US$115bn in six years' time. Furthermore, the value of nano-materials supplied to textile industry will reach US$8,6bn by 2012.

In terms of end use, nanotechnologies will see the highest growth in non-traditional sectors which include sports/outdoor textiles and technical textiles- although fabrics for clothing textiles will still make up the largest share of the total textile market. So, it seems that the backlash against the use of nano-particles in other industries such as cosmetics is unlikely to impact on textiles, and if the findings of this research put over time, the business benefits of these minute particles look like being huge.

Because of all mentioned developments in nano-technology, functional aspects for clothing textiles, which promote the wearing comfort and well-being, have become a striking sales argument. With an innovation like never before the development of "textile with function" are being pushed.

Therefore, the numbers of the researches in "cosmetic effects of clothing textiles" have started to get increased. The main reasons why clothing textiles need cosmetic effects are [4]:

- Body care (not only face and hand care) is one of the major trends in cosmetics.
- Textiles cover a large part of the body for most of the day, which means a unique opportunity for the convenient transfer of cosmetics to large parts of the body.
- Continuous release of small doses of cosmetics may be more effective than single applications of large amounts of well-known drugs.
- Consumers are increasingly interested in and open to textiles with added effects: functional garments are massive trend in textile.

On the other side, cosmetic effects of the clothing textile have been facing with some technical challenges in recent. The main challenges to attach cosmetic ingredients onto textiles in such a way that

- They are not destroyed in the finishing process.
- They remain stable during storage.
- They are not washed out during further launderings.
- They are transferred to the skin while the textiles are being worn and can therefore produce real controllable effects.
- The main technical challenges are the washing permanency and the controlled release properties.

Microencapsulation is the key application process of attaching the cosmetic ingredients onto textiles. In this thesis, microencapsulation process details as well as the technical challenges of the application of microcapsules onto the clothing textile is examined. It is aimed to improve the release properties and laundering durability of the microcapsules. Different type of recipes was applied by both exhaust method and foulard method onto the fabric and the laundery durability performance was analyzed by using scanning electron microscope (SEM). In the literature, it was found out that there was no any research in the area of improving laundering durability by using chitosan coating process. Therefore, in this thesis, via foulard method, the performance of the laundering durability of chitosan coated microcapsule treated fabrics was examined. Furthermore, to make a numerical performance data comparison between the application methods and recipes, a gas-chromatographic analysis was also conducted.

2. LITERATURE SURVEY

2.1. Microencapsulation Processes and Implementation Areas

Insect repellents, anti-cellulite treatments, and anti-microbial agents for medical textiles are just a few of the features which clothing manufacturers are using to add value to their ranges, using microencapsulation techniques, according to the latest issue of Performance Apparel Markets [5].

This innovative technology makes use of microcapsules that act as tiny containers of solids or liquids. These containers release their core contents under controlled conditions to suit a specific purpose. Microencapsulation is already used to impart a wide range of features, including:

- Thermo chromic and photo chromic dyes, used to make garments which change colour when they are exposed to temperature changes or sunlight;
- Anti-microbial and deodorising finishes, offering great potential for freshness retention during wear for intimate apparel, and for garments worn during periods of strenuous activity;
- The controlled release of active substrates, offering opportunities in the medical textiles field;
- Insect-repellent and insect-resist treatments, demonstrating higher levels of performance if microencapsulated;
- Finishes which effectively deodorise the retention of odours such as tobacco smoke, offering a further contribution to easy-care in apparel;
- Flame retardant finishes, with improved durability of the treatment to leaching, domestic washing and dry cleaning; Enhanced chemical protection, for the military and other users, particularly for chemical decontamination of hazardous chemicals and chemical warfare agents; and
- Cosmeto-textiles, capable of imparting skin care benefits, combating ageing, and promoting a feeling of wellness or well-being.

Microencapsulation of flame-retardants is now at the research stage. Significant development work will lead to performance apparel offering enhanced protection against heat and flame. Similarly, research and development could lead to improved protection against chemical warfare and hazards [5].

Microencapsulation technology is still relatively new to the textile and apparel industry. However, greater awareness of the benefits of the technology for performance apparel will emerge as chemical manufacturers target specific enhancements in apparel performance and focus their marketing effort accordingly.

Reviewing the various types of intelligent textiles, the major concept for functionalising textiles, which can be retained, is the use of microcapsules, either or combined with laminating and coating processes or with printing, dyeing, or finishing processes [6].

Microencapsulation is a micro-packaging technique that traditionally involved the deposition of thin polymer coatings on small particles of solids, droplets of liquids or dispersion of solids in liquids. The ingredients to be encapsulated are referred to as core, internal phase, active, encapsulate, payload, or fill; whereas terms applied to the coating of the micro-capsules include wall, shell, external phase, or membrane. The technique was primarily established as the basis for the carbonless copy paper industry and is now used widely in a number of industries. Research aiming at incorporating cosmetic compositions into textiles started to intensify in the late 80s. One of the important patents in Europe was described as “an invention relating of microcapsules encapsulating a substance having a function to improve physiological conditions of human skin..., treating liquids containing such microcapsules; and textile structures treated with such a treating liquid″. According to the patent, microcapsules contained on textiles are typically prepared according to the following process:

1. Encapsulation of a cosmetic of medical formulation, preferably by in-situ or interfacial polymerization of urea-formaldehyde resin;
2. Fabric treatment with “water repellent” to minimize its subsequent stiffening because due to binder penetration;
3. Application of microcapsules with a binder, preferably silicone or polyurethane based, from an aqueous dispersion;
4. Drying or heat setting.

In more general terms, micro- or sub-micrometer dimensioned hollow bodies may be created similar to natural ones (e.g. Golgi vesicle). The simplest forms are those in which the walls are single-layered. The manufacturing principle is as follows; a finely dispersed solid is suspended in a polymeric solution; drops are then formed and further hardened. The wall is thus the continued phase of the particle and the solid is embedded in a polymeric material, forming a continuous matrix. In fact, there are over 50 different known wall materials; both natural and synthetic polymers can be used to form microcapsules. These include the natural polymers gelatine, gum arabicum, carrageenan and alginate, and synthetic polymers such as ethyl cellulose. The finished capsules can be modified by cross-linking further depositions of layers of wall material, dyeing, waxing, and grafting. The range of commercial microencapsulation techniques fall into six distinct categories:

2.1.1. Commercial Microencapsulation Techniques

There are six commercial microencapsulation techniques in the market (Table 2.1)

Table 2.1: Commercial Microencapsulation Techniques [6]

1. Spray coating methods		
Processes	**Principles**	**Chemicals**
Pan coating Fluid-bed coating Wurster air suspension coating (Coating Place)	Batch processes where fine particles are encapsulated, as they are suspended in an up-wards-moving air stream. The coating solution is sprayed on the particles; the wall materials harden onto particles.	Wall materials used are e.g. sugars, gums, cellulose derivatives, and other materials such as chitosan
2. Wall deposition from solution		
Processes	**Principles**	**Chemicals**
Complex coaservation (Euroband)	The process of complex coaservation (i.e. involving more than one colloid) consists of four separate stages; each stage is carried out under continuous agitation. First, the core material is dispersed within the wall material, which is in liquid form. Three immiscible chemical phases are than formed by changes in pH, temperature, ionic strength, or the addition of non-solvent or an incompatible polymer. The coating material is then deposited on the core materials by means of further physical influences. Cross-linking, thermal curing, or desolvatation finally hardens the liquid polymer on the surface of the core.	The technique can be used to encapsulate water-soluble and water-insoluble liquids, solids, or dispersions – e.g. gelatine in gelatine/gum arabicum.
3. Interfacial reaction		
Processes	**Principles**	**Chemicals**
Interfacial polyconden-sation Isocyanates process	An active agent (e.g. pesticide) is dispersed in an organic diacid chloride by mechanical agitation in water. The emulsion formed is stabilized using a surface-active agent. Once the appropriate droplet size is achieved, an aqueous solution of a daimine	The walls are formed by reaction of organic diacid chloride and a daimine. Hardening can be increased by the

Parlene free radical condensation Alginate polyelectrolyte membranes Direct olefin polymerization Surfactant cross linking Clay-hyroxy complex walls (Ryan) Protein cross linking (Frippak)	is added. Isocyanates are often added to increase hardening of the capsules by cross-linking the wall material. The capsules can be dried, although formulation into stable liquid suspensions by adding appropriate thickening or suspending agent is more common. The active agent is released by simple diffusion or by passage through microscopic pores.	addition of isocyanates. The core includes the active agent as well as surface-active agents. Additives such as UV absorbers and antioxidants that are soluble within the oil phase and do not interact with the building blocks of the wall material may be also be included within the capsules. Formulation additives can be thickeners, or suspending agents (emulsifiers).
4. Physical processes		
Processes	**Principles**	**Chemicals**
Vacuum metallisation Annular-jet encapsulation (SWRI, 3M) Liquid membranes (Exxon) Gas-filled capsules (Materials Technology) Fast-contact process (Washington University)	These processes involve nozzle devices. E.g. a fluid core material is pumped through a central tube while liquefied wall material is pumped through a surrounding annular space. The extruded rod of material then breaks up into droplets. Hardening takes place during passage through a heat exchanger. The immiscible carrier fluid is subsequently filtered, reheated and recycled.	Fluid core material Liquefied wall material Immiscible carrier fluid, solvent, or air
5.Matrix solidification		
Processes	**Principles**	**Chemicals**
Spray drying	A combined solution of core and wall material is atomized using spray techniques. Hardening is obtained by evaporation of water or other solvents, or by cooling if wall materials are made of fa tor wax. Air stream carries the solid capsules along until separation takes place in a cyclone. Further cleaning may be necessary involving filtration, scrubbing, or incineration.	The solution of the core/wall materials can contain water or other solvents. The wall materials can be, for example, a melt of factor wax, although other materials are also possible.
6. Naturally occurring pre-formed capsules		
Processes	**Principles**	**Chemicals**
Encapsulation of fat-soluble materials using yeast, filamentous fungi or protozoa	Some micro-organisms (especially yeast) have the property of accumulating fat within their cells when growing on specific media (up to 40-60% fat weight). Proteolitic enzymes could be added to aid release by softening the capsules. Hardening can be obtained by cross-linking of the cell wall material using formaldehyde or glutaralhyde.	Examples of yeast are Torulopsis lipofera, Endomyces vernalis, and Saccharomyces cerevisiae; Fat-soluble substances, which can be incorporated, are dyes, lubricants, flavours, aroma compounds, and adhesives. Cross-linking agents and softening enzymes are further additives of the processes.

Encapsulation of dyes using lipid-extending substances and yeast (Dunlop)	Yeast with more natural fat content (i.e. less than 40%) are used to encapsulate core material such as dye. The dye must be soluble or freely dispersible within a so-called lipid-extending substance to be absorbed by the yeast, as a component of the core material.	Lipid-extending substances such as e.g. aliphatic alcohols C_4-C_5 have been employed to prepare cells containing leuco dye. (cf preparation of carbonless copy paper.)
Refined Dunlop process (AD2, Birmingham)	Yeast containing low levels of fat (less than 10%) can be used as microcapsules without so-called lipid-extending substances. Yeast cells incubate at elevated temperature in small volumes of solution or dispersion of core material. The core material is able to diffuse across the yeast cell wall. It has been proposed that an unknown natural surfactant present in the yeast aids the encapsulation process. The products can remain as a suspension or dried. The contents of the capsules are released by simple diffusion or by subjecting the cells walls to physical pressure, or chemical or microbial attack.	The solvent used is usually water, but other solvents such as ethanol or isopropanol can also be used. Treatments of wall material by proteolytic enzymes or chemicals such as sodium hyroxide or magnesium salts increase the permeability of the cells. The list of possible core materials is almost endless but includes flavours and fragrances, pheromones, insecticides, dyes, vitamins, drugs, detergents, rodenticides, nematocides, insect repellents, herbicides, fungicides, molluscicides, insect and plant growth regulators, as well as food colorants.

Different encapsulating processes for textile purposes are possible, depending what kind of particle properties are needed [7]:

- Spray drying (perfume oils in gum arabic);
- Hardened emulsion (core: enzyme; wall: polystrol, ethyl cellulose, silicone);
- Building of liposome's (phospholipid vesicles);
- Complex coaservation (gelatine and gum arabic), i.e. the core material is emulgated in a gelatine/gum arabicum solution which further partially precipitate (coaservate formed by pH influence) and orient themselves around the core particles. The hardening of the gelatine/gum arabicum walls occurs by decreasing the temperature (gelatinising) and adding formaldehyde or glutaraldehyde
- Surface polymerisation (carbonic acid chloride and amine or alcohol; polyester, polyurea, polyurethane), for example, the formation of polyurea capsules made of polyisocyanates, occurs immediately after the addition of cross-linking agent based on polyamine. The polyisocyanate dispersed in oil drops reacts on its surface with the cross-linking agents to form polyurea wall material.

- Self organisation, a deposition in layers of polyelectrolytes (e.g. sodium polystryrol sulphonate and cationic polyelectrolyte) on a supporting substrate. Layers of 10 to 100μm are prepared and further dissolution of the substrate may transform the coated particles in hollow balls (≅4 μm) (e.g.melamine-formaldehyde core can be dissolved in acidic solution of pH<1.6). The diffusion of the core particles (of nearly 1nm) proves that the formed membrane is permeable. A core made of polytryrol latex can be destroyed by heat;
- If smaller particles are wished, block copolymers are synthesised and further arranged into polymer micelles. Polymeric micelles having a diameter ranging from 10 to 100 nm are made of polyisopren and polystrol as core material and polyacrylic acid and poly(tertbutylacrylate) walls. The envelope remains semi permeable, even after cross-linking.

The aim of the encapsulation process is to isolate the core material from the environment. However, a release of the core material must occur during use. Most particle walls can be destroy through application of pressure or gravitational force; others by the action of solvents, enzymes, chemical reactions, hydrolysis, or slow abrasion. The mechanism of controlled release replaces the process of repeated metering of non-capsulated systems; and thus decreases their toxicity potential by avoiding high starting concentrations.

The microcapsules used in the textile industry are typically of diameters from 2 to 2000 μm and have wall thickness of 0.5 to 150 μm. The proportion of core material in the capsules is usually between 20 and 95% per mass; however, there may be applications where lower levels of encapsulant are desired. Microcapsules are generally manufactured in the forms of free-flowing powder, although some commercial preparations are suspensions or even solid cakes or bricks of material.

The capsules are used, for example, in colouring (dyeing and printing) processes and for hygienic, deodorizing, and medical purposes. Encapsulated perfumes are especially used for application on nonwoven fibers, however, application of embedded biocides on textile products such as underwear, socks and sportswear, etc. are also common today [7]. Other applications include dyes, vitamins, skin softeners, phase change materials, etc [8].

2.1.2. Main Textile Applications of Microencapsulation

Table 2.2: Main Textile Applications of Microencapsulation [6]

Application fields	Properties
Dyeing and printing textiles	Microcapsulated dyes and pigments, duplex multicolored fabric, transfer printing, electrical colouring etc.
Hygienic, deodorant, and medical uses	Fragrance, insect repelling, cleaning, antimicrobiotic, cosmetic, aromatherapy, flame-retarding etc.
Textile processing	Delayed-cure systems for easy-care finishing, systems for high-secure handing, formation of functionalised fibers, etc.
New application fields	Bioreactor systems, colour-changing effects, functionalised hosiery, military applications, etc.

The use of encapsulated dyes in dyeing or printing processes presents several advantages (Table 2.2.) Classical transfer printing is usually limited to the use of dyes able to volatize at temperature lower than the melting point of the textile. This restriction can be surmounted by encapsulated dyes able to be released by pressure or chemical action can be a solution to surmount the restriction. The application field is especially interesting when printing with transfers on polyester and polyamides. Another application field of encapsulated dyes in the dyeing process is to obtain multicolored specks effects on textiles. Disperse dyes encapsulated in methylcellulose are marked for dyeing polyester (e.g. Fine Colour N Type, Matsui Shikiso Chemical Co.). Other disperse dyestuffs are encapsulated in gelatine, pectin, agar, methylcellulose, acrylic or maleik acid. Multicolored effects can be obtained on polyester, cotton, acrylics, polyamide, and wool (e.g. MCP HP Dyestuffs, Hayashi Chemical Co.). Colour specks of 50-3000 μm in diameter are obtained. For dyeing textiles using aqueous method, the capsule walls must be hydrophilic, thickening agent are required to control dye diffusion through capsule walls. The capsules containing disperse dye are 10-200 μm in diameter can be ruptured on steaming. On preparing dye liquor a suitable carrier must also be added, dye and carrier do not come into contact. Yet, rotary-screen printing was also adapted for encapsulated dyes, by increasing the mesh of the screen. Moreover, filtering the encapsulated dyes and further addition of thickener in the paste is recommended. Although basic and

acid microencapsulated dyes are available, these types can so far only be used to produce small-multicolored specks by single-phase printing. Textile fabrics with dual surfaces of different colour tones can also be produced using microencapsulated printing technique (i.e. duplex multicolored fabric, on both sides) [9].

Mixing microcapsules containing dyes, with other containing fastness-improving agent, can also combat undesired migration of the dye in textile processing. Dyes are encapsulated 30% (by mass) of the polymeric wall material and fastness agents (e.g. sodium carbonate) with 60% (by mass) achieve best results. The wall materials used include methylcellulose, poly acryl amide, and carboxymethylcellulose (Fuji Photo Film Co.). The capsules (20-200 μm diameter) are ruptured on heating, releasing dye or fastness agent. A different approach to the problem is the in situ preparations of microcapsules during screen-printing and other colorant process. For this Miliken Research Co, developed a method where the textile material is first pretreated with an aqueous solution containing a skin-forming ionic component. Examples such components are anionic ones like bipolysaccharides, poly (acrylic acid) and anionic acrylic copolymers. Cationic ones can be polyacrylamide copolymers. The application amounts of the ionic polymer are 0.5-5.0 % by mass. The textile material may be then dried and the dye liquor made of acid, disperse or direct dyes added. Additive of the liquor is an ionic component of opposite charge to the primary treatment. A water-insoluble dye-impermeable skin around the individual dye droplets is thus formed by ionic interaction. Thereby, unwanted migration of the dye is controlled. The process can be used to pattern dye on whole range of material such as natural and synthetic ones. It can also be incorporated into jet-injection printing. Release of the dye is controlled by application of steam, thus melting the capsule walls. [9].

Printing on textile using electric fields can be performed using dyes particles encapsulated in a wall material having dielectric properties. Dispersing agents and solvents are not usually required but can be co-encapsulated with dielectric liquid if required. Suitable wall materials include vinyl resins such as poly acrylate and polyacrylamide, polyester resins and polyamide resins. Numerous dye types can be used for printing on knitted or nonwoven materials made of wool, polyester, regenerated cellulose, cotton, ect. The dye carrier liquid can be water, alcohols such as methanol, ethanol or propanol, or ethylene alcohols. Rupturing of the capsules

(less than 50 mμ diameter) is achieved by means of pressure, heat, or appropriate solvents. The advantage of method is that no further addition of rigid resin binder is necessary to ensure fixing of the dye on textile [9].

The 3M Company has developed a novel transfer printing technique using microcapsulated system that can release colorant by simply rubbing of the transfer paper on to the target textile material. Up to 50% of the colorant is bound to the exterior surface of the microcapsule, to enable a small time delay between rupturing of the capsules and colouring. A wetting agent enables the colorant to be carried from the material containing the bound microcapsules. The hydrophobic inner phase of the microcapsules may be fragrant oils, mineral oils, triglycerides such as castor oil, plasticizers such as phthalate esters, or polybutene. The most common preparation process of the capsules (10-80 nμ) is aminoplast polymerization [9].

Further examples of encapsulating are the use of liposomes during dyeing process of wool. In recent years, liposomes have been examined as way of delivering dyes to textiles in cost-effective and environmentally sensitive way. Amphipathic lipid molecules may form double-layered lipids, due to their tendency to rearrange themselves. The vesicle formed may be multilamellar (MLV) where the layers are spaced by liquid, unimellar (ULV, 100 mμ), or small vesicles (SUV, <100nm) [7].

Liposomes are prepared using a liquid or combination of lipids; most commonly, phospholipids such as phosphatidycholine are used. Especially for application on wool, the liposomes can also contain lipids such as cholesterol in wool lipid. Several procedures can be used to prepare liposomes including thin film hydration, sonification, and extrusion, use of French press, ethanol injection, detergent dialysis, or reverse-phase evaporation. Recent studies conclude that wool dyeing using liposomes is cost-effective and reduce fiber damage by permitting a lowered dyeing temperature. Liposome concentrations of 1% allow dye bath exhaustion greater than 90% at low temperature of 80 ^{0}C. Moreover, there was a significant saving of energy costs and impact of the dyeing process on the environment was also reduced, with chemical oxygen demands being reduced by about 1000 units [8].

Hygienic, deodorant, and medical uses are certainly bearing the most diverse application field. A large variety of ingredients have already been incorporated in microcapsules. Water-insoluble materials such as fragrances or insect repellents were

encapsulated by dispersing in coating solvents or mixing them in aqueous systems containing appropriate additives (e.g. viscosity builders/ thickeners, surfactants). The microcapsules are sprayed onto nonwoven material with a binder such as PVA or acrylic, and adhere between the strands of the fabric. Coating weights of between 2 and 30 g/sqm have been achieved, yet, leaving the surface characteristics unchanged [9]. As well as fragrance and insect repellents, disinfectants and cleaning agents can be included. This coating technique can also find use by application on other textile materials, especially in the case of special work wear, etc.

Microcapsules incorporated into sizing bath or other finishing liquor is already obtainable. Fragrances such as lavender oil or pine oil have been encapsulated in gum arabicum and gelatine capsules. Yet, other encapsulated essential oils (e.g. apple spice) were also impregnated onto numerous textile materials, for so-called aromatherapy (Kanebo Ltd). The microcapsules (5-10 μm) are attached to the fabric as an extra process at the end of fabric dyeing. For example, a pair of stockings would contain approx. 200 million fragrant microcapsules and persistent well smelling to hand washing up to ten times. Other incorporated materials e.g. herb armur cork (Phelodendron amurense), vitamin C, seawed extracts, antimicrobial agent, and insect repellent.

Fragrant fibrous materials have also been produced that consist of perfumes bound to variety of fibers using a low-temperature reactive organopoly-siloxane resin. Urea-formaldehyde or melamine-formaldehyde have been used as wall materials to prepare capsules that contain approx. 90% by mass of perfume such as jasmine oil or sandalwood oil. Soaking, padding, coating or printing, and further curing of the resin apply the capsules. However, a pretreatment of the textile material with water-repellent agent such as wax emulsion to prevent penetration of the binder (i.e. preferably silicone binders) into textile material. In fibrous structures that are treated with polyurethane elastomers, such as nonwovens or knitted fabrics, no resin binding stage is necessary as the microcapsules can incorporated into the elastomers before application; resin are also unnecessary where fiber composites are employed [9].

Capsules made of yeast (wall) and mothproofing agents (core) are used to obtain a permanent hygienic finish on textiles. The yeast serves as nutrients for the moth and the active ingredients are released by eating. Microcapsules containing fragrance may be applied via a binding agent as disperse paste on cotton, polyester, or

polyamide. Two major techniques of incorporating water-insoluble or fat-soluble ingredients into microcapsules were described. (Table 2.1.)

The ingredients used were alkali-soluble biocides (e.g. dichlorophen), water-insoluble biocides (e.g. Kathon 893) and essential oils (e.g. mint, clove, cedar oil). [9]. The traditional "scratch and sniff" application of fragrance containing gelatine or synthetic capsules was made using screen printing, litho, or web printing techniques. Systems comprising aqueous dispersions of encapsulates can be applied by pad, exhaustion or hydro extraction techniques to a wide variety of substrates. Durability to washing and handle (or feel) may be further improved by incorporating suitable formaldehyde-free binders and softeners. For screen-printed applications, the microcapsules are simply mixed with water-based, solvent-free inks or binders. Once printed, the fabric is then cured, as with standard textile inks, to achieve a good bond to the fibers. Usually a softener is also required, as unsoftened fabric containing microcapsules can sometimes appear to be stiffened. The microcapsules prepared using melamine-formaldehyde systems show, when attached to cotton, that the smaller the capsules, the better they survive laundering. The phenomenon may be due to the relative thickness of a capsule within an adhesive film binding the capsules to the textile substrate [8].

The use of the microencapsulation processes in detergent formulations is widespread, principally for the protection of sensitive ingredients during storage and for prolonging the activity of ingredients such as enzymes during wash cycle. A novel product type is a kind of transfer cloth or felted sheet that must be added during garment laundering. The transfer cloth contains encapsulated perfumes or deodorant, which become entrained in the fabric and enter the pores of the garment. The active ingredient can further released by physical pressure during common wearing. The wall of the capsules (10-200 μm diameters, 0.1-10 μm thick) is made of urea-formaldehyde polymers and has loading of perfume oil over 50% by mass. [9].

Manufacturing fibers with hollow center core is one way of utilizing microencapsulation technology in textile industry without affixing microcapsules to textile material. The fibres are thus made with identical or at least similar process and materials as for microcapsules walls (Table 2.1) and exhibit the same release characteristics. For example, fibres made of polyethylene core containing aromatic perfumes or essential oils (for up to 10% of the mass) and coated with polyester sheet

are still marked (Mitsubishi Rayon Co.). Other examples are the fibers marked under the trade name Accurel ® (Enka/Akzo group). The matrix material is polyolefin's such as polyethylene, polypropylene and poly (vinylidene fluoride), yet, copolymers such as ethylene/acrylic acid salts and condensation polymers such as nylon 6, polyactidiacid and poly(ethylene oxide) can also be used.

The matrix is different of other encapsulation systems in that the material is micro porous, the pores on the capsules and the fiber surface being between 0.1 and 1.5 µm in diameter. Within the capsules the pores are interconnected giving sufficient internal space for incorporation of 75% core material by mass. Supplies of the products can be obtained with or without core material [9]. Another fiber is based on polyacrylonitrile (Actipore ® by Focus Polymers, Courtaulds group) and can incorporate as active agents silver nitrate (0.5% by mass), polyvinylpyrrolidone-iodine complex (0.92% by mass), copper chloride (15% by mass), chlorohexidine and its salts, hydrocortisone and other transdermal drugs, non-adherent for wound dressings, and Ionalin. Tetracycline and polyvinylpyrrolidone-iodine complex have also been incorporated in fibers formed from polycaprolactone (biodegradable), polyethylene and polypropylene (both non-biodegradable), with up to 25% by mass of active ingredient [9].

An important application field of microcapsules in textile processing is the market of easy-care articles of natural regenerated cellulose fibers. Fabrics are treated with cross-linking agents and/or catalysts during finishing, but the resin formation only occurs after fashioning of the garment (so-called delayed-cure). The system has to be stable during storage and transport. Microencapsulation of the reactants ensures that less care is required in selecting the appropriate cross-linking material, as the capsule wall protects the reactants from chemical attack and inhibits the release of volatile or malodorous ingredients (e.g. formaldehyde). The capsules employed are between 75 and 175 µm in diameter and, as the capsule walls are made ethyl cellulose, the residue of the wall material after curing contributes to the physical properties of the fabric (i.e. functions as fabric softener).

Custom-made microcapsules were also manufactured for use in non-aqueous solvent systems (e.g. Kanegafuchi Boseki Kabushiki Kaisha Co.). The capsules contain solutions of hydrophobic agents for treating textiles i.e. anti-pilling agent, softening agent, felting agent, UV absorber, anti-static agent, anti-soiling agent, water-repellent

agent, cross-linking agent or colorant. The wall materials, formed by interfacial polymerization, are prepared using polyurethane's, silicone resins, polyamides, epoxy resins, polyamides or polyester, and have low breaking strength [9].

Microcapsules (1-10 µm) have also been prepared by using phase separation technique which can be incorporated into spinning solutions and, thus, being incorporated into an extruded fibers. More generally, core materials that are chemically, thermally or mechanically unstable can be encapsulated with amounts of 0.5% to 40% by mass. A number of polymeric substances have been used including gelatine, ethyl cellulose, polyester and polyamide as wall material. Using both wet and dry-spinning techniques from well-known fiber forming polymers, including polyamides, vinyl polymers, acrylic polymers and polyacrylonitriles can form fibers. The core material incorporated into these fibers includes flame-retardants, deodorants, softening agents, perfumes, anti-static, antioxidants and UV absorbers (e.g. Exlan Co. process) [9].

New application fields of miscellaneous microcapsules are given in the following; paraffin wax which changes from liquid to solid state (and vice versa) solely due to change in temperature are so-called Phase Change Materials (PCM). PCMs such as nonadecane ($C_{19}H_{40}$) and other medium chain-length alkanes are microscopic in size and are contained in an outer plastic shell, which is very durable (1µm thick, 20-40 µm diameter; loading of 80-85%PCM) [8]. PCMs are incorporated into fiber, coated on fabric, or topically applied to foam in order to obtain thermal adaptive functions for the items. The phase-change polymers adjust, absorb, and store excess heat during sport activity for example, and release it further if necessary ("body equalization process") [10]. Yet, there are number limitations when using microencapsulated PCMs. For PCMs incorporated into fibers, the only currently available commercial fiber is acrylic, and there is an upper limit to the amount of PCM in the fibers, beyond which the fibers tensile properties are appreciably reduced. Where PCMs have been coated on to fabrics, fabric handle may be compromised, and durability to abrasion during wear and to washing and dry-cleaning may be lowered [11].

New concepts are systems made of shell and core materials capable of "controlled release" of the ingredient in the capsules. This can be obtained by activating, with e.g. light, ultra waves, or temperature, and inactive encapsulated substance. These

new systems will be optimized for application on both synthetics and natural fibers [7].

Other applications of microcapsule technologies are colour-changing systems. Colour-changing systems are beginning to be seen in the textile applications such as product labeling, medical and security applications, and novelty textiles for purposes such as swimwear and T-shirts. The two major types of colour-changing systems are: thermo chromic, which alters colour in response to temperature, and photo chromatic, which alters colour in response to UV light. The colour-changing materials are produced in an encapsulated form, which protects the sensitive chemicals from the external environment. Today, dyes are available which change colour at specific temperatures for a given application. Physicochemical and chemical processes such as coaservation and interfacial polymerization have been used to microencapsulate photo chromic and thermo chromic systems (Fig. 2.1. and Fig. 2.2). Interfacial polymerization techniques are the most popular, as they produce durable capsule walls. The most widely used capsule systems for inks involve urea or melamine-formaldehyde shell formation. Microencapsulated colour-changing dyes can be applied to textiles using a variety of printing processes, including screen-printing and gravure printing. Thermo chromic dyes are made of specific liquid crystals for precise colour modifications, or specific leuco dyes if a response over a more general range of temperatures is needed [8].

The most important types of liquid crystals for thermo chromic systems are the cholesteric (chiralnematic) types, where adjacent molecules are arranged so that they form helices. Thermochromism results from selective reflection of light by the liquid crystal. An alternative means of inducing thermochromism is through the rearrangement of the molecular structure of a dye, as a result of a change in temperature. The most common types of dye, which exhibit thermochromism through molecular rearrangement, are the Spiro lactones. In reversible thermo chromic systems a colourless dye precursor and colour developer are both microencapsulated along with a non-volatile, hydrophobic organic solvent. The colour developer can donate a proton to the dye precursor, reacting thus to form the dye itself. On heating, the solvent melts, whereupon the microcapsules become colored or lose colour. The reverse change occurs if the mixture is then cooled [11].

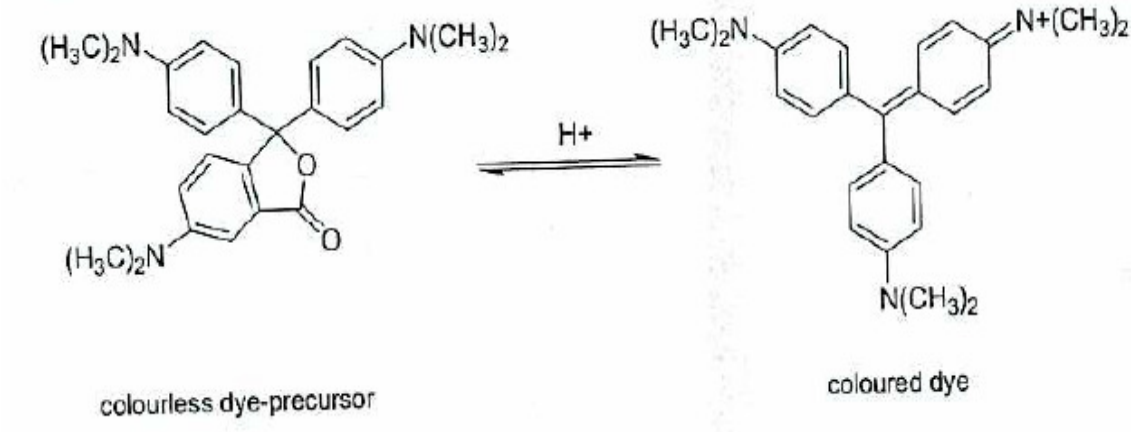


Fig. 2.1: Example of Spirolactone Dye Used in Thermo-chromic Microcapsule Systems [6]

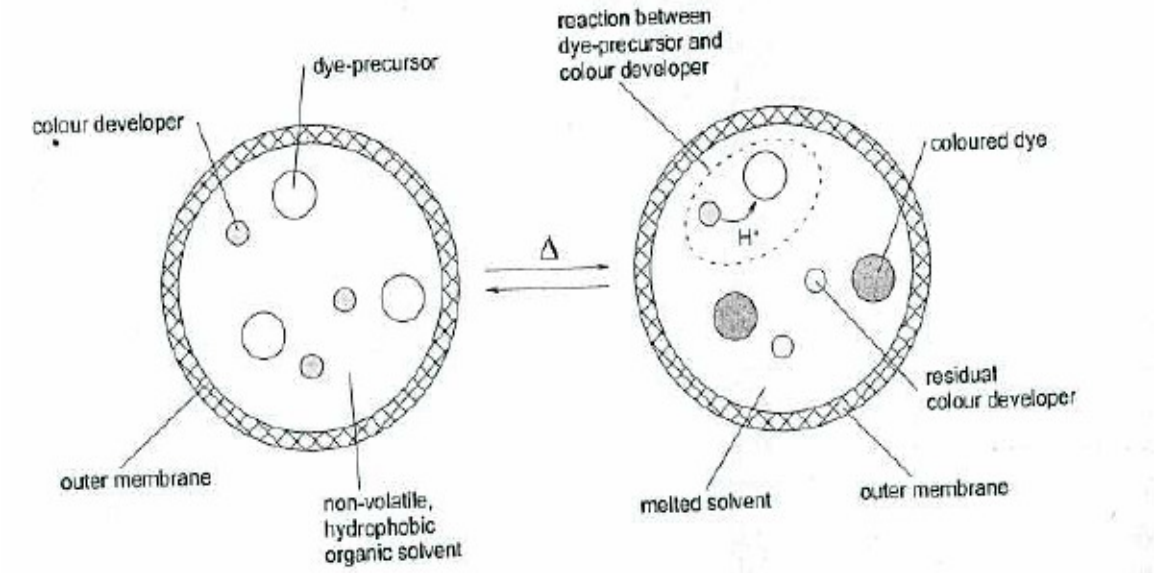


Fig. 2.2: Schematic Representation of a Thermo Chromic Microcapsule System [6]

Polychromatic artificial yarns and fibers have also been prepared by incorporating liquid crystals into the internal cavity of a yarn or fiber. The fibers consist of a transparent outer surface and an internal tube that contains an aggregation of microcapsules with a liquid crystal care material. UV absorbs such as iron (III) oxide are co encapsulated to reduce damage to the liquid crystals. The fibers can be knitted or spun and can be mixed with a variety of other fibers to produce interesting products (e.g. Kyoshin Sangyo Co.) [9].

Microencapsulation does not protect the dyes completely from the elements, and eventually the properties are lost (usually after 6 months). Particular care must be taken with the solvent and other components within the ink mix [8]. Photo chromatic and polychromatic dyes are also available as encapsulated formulations on textiles. Newer technologies have been developed including hydro chromic dyes, which

change colour in contact with water, and piezo-chromic dyes, which change colour in response to pressure.

Another interesting application of microcapsules is their use in flame retardant finishing. Both flame-retardants and intumescents can be encapsulated using a poly (vinyl acetate) resin and applied to textiles, and thus, overcome the usual disadvantage of conventional finishing with flame-retardants. The resin also acts as the adhesive for attachment of the capsules to the fabric, usually cotton alone or in blends with nylon or polyester. Other systems incorporate the microencapsulated fire retardant during spinning of polyester fiber for blending with cotton. It was found that microencapsulation in silicone-containing shells, in particular, vinyl-triehoxysilane, produced significant advantages in decreasing combustibility in poly (ethylene terephtalate) [8].

Microcapsules have also become interesting for military applications. The decontamination agent, consisting of 90% syn-bis (N-chloro-2, 4, 6-trichlorophenyl) urea and 10% zinc oxide, has been encapsulated in ethyl cellulose wall material, employing interfacial polymerization and phase separation techniques. The microcapsules (content of 75% by mass) have been bonded to fabric using acrylic binders in a resin finish. Irreversible decontamination of mustard gas takes place when the gas diffuses into capsules. Polyamide capsules containing other decontamination agent such as monoethanol amine and the hypernucleophilic agent 4-(NN-dimethylamino) pyridine were also prepared for deactivation of the nerve gas Sarin. [9].

Microcapsules used for combating textile counterfeiting contain a colour former or an activator applied to, for example, a thread or a label. The microcapsules are applied using printing techniques onto a label as a logo or another printed message. They adhere to the textile and, depending on the type of chemical within the capsules, can be detected at a later date to check the authenticity.

Miscellaneous applications are uses such as bandages and support hosiery treated with capsules containing glycerol stearate and silk protein moisturizers. The textiles are in direct contact with skin and thus extensive medical treatment is obtained allowing high comfort and skin quality. Further application of microencapsulated

octane, tung oil and paraffin oil as cleaning solvents is reported for producing cleaning/wiping clothes made of polypropylene nonwoven material.

Yet, the use of alternative insecticidal compounds such those found in many essential oils and other plant extracts is reported for production of long-lasting acaricide bed sheets [9].

Swapan Kumar Ghosh [12] has made some researches about functional coating and microencapsulation processes as well. In according to Swapan Kumar Ghosh, Microencapsulation cannot be defined as a product or as component of a product. Rather, it is described as a process of enclosing micron-sized particles of solids or droplets of liquids or gasses in an inert shell, which in turn isolates and protects them from the external environment. The inertness is related to reactivity of the shell with the core material. This technology is mainly used for the protection, controlled release, and compatibility of the core materials. A microcapsule is shown schematically in (Fig. 2.3 and Fig.2.4)

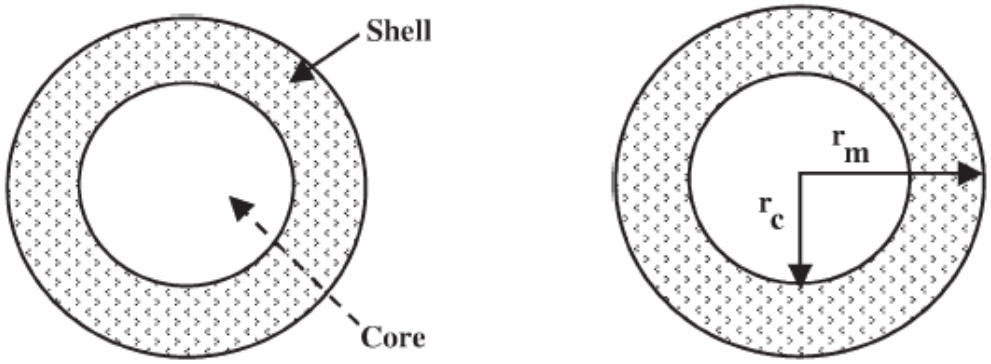


Fig. 2.3 and **Fig. 2.4** Schematic of Microcapsule and The Right One is the Cross-section of an Idealized Microcapsule [6].

The abundance of natural and man-made polymers provides a wider scope for the choice of shell material, which may be made permeable, semi-permeable or impermeable. Permeable shells are used for release applications, while semi-permeable capsules are usually impermeable to core material but permeable to low molecular-weight liquids. Thus, these capsules can be used to absorb substances from the environment and to release them again when brought into another medium. The impermeable shell encloses the core material and protects it from the external environment. Hence, to release the content of the core material the shell must be ruptured by outside pressure, melted, and dried out, dissolved in solvent or degraded

under the influence of light. Release of the core material through the permeable shell is mainly controlled by the thickness of the shell wall and its pore size. The dimension of a microcapsule is an important criterion for industrial applications.

Assuming that the density of the core (ρ_c) and shell (ρ_s) materials are identical

(i.e., $\rho_{c=}\ \rho_{s),}$ it is possible to establish the relationship between the shell thickness

($d_s= r_m-r_c$) and the ratio of the weight of the shell material (w_s) to that of the core material (w_c):

$$ws/wc = (4/3)\pi\ (\ r^3_m - r^3_c).\ \rho_s\ /\ (4/3)\ \pi\ r^3_c.\ \rho_s \qquad (2.1)$$

After rearranging, the following equation is obtained:

$$d_s = (r_m-r_c) = [[(ws/wc) +1]^{1/3}-1].r_c \qquad (2.2)$$

Equation (2) shows a linear relationship between the shell thickness and the capsule diameter when the ratio of $w_c/ (w_s+w_c)$ is in the range of 0.50 to 0.95 [13].

Numerous preparation technologies available for encapsulation of core material have been reported [13-15]. The present discussion focuses on the different microencapsulation techniques that more relevant to the coating industries and also provides a comprehensive review of recently developed methods. In general, microencapsulation techniques are divided into two basic groups, namely chemical and physical, with the latter being further subdivided into physico-chemical and physico-mechanical techniques. Some of the important processes used for microencapsulation are summarized in Table 2.3.

Table 2.3: Different Techniques Used For Microencapsulation [12]

Chemical Processes	Physical processes Physico-chemical	Physico-mechanical
• Suspension, dispersion and emulsion Polymerization • Polycondensation	• Coacervation • Layer-by-layer • (L-B-L) assembly • Sol-gel encapsulation SupercriticalCO2-assisted microencapsulation	• Spray-drying • Multiple nozzle spraying • Fluid-bed coating • Centrifugal techniques • Vacuum encapsulation • Electrostatic encapsulation

2.1.3. Chemical Methods

In-situ process such as emulsion, suspension, precipitation or dispersion polymerization and interfacial polycondensations is the most important chemical techniques used for microencapsulation. An image of microcapsules with an aqueous core and silicone shell prepared using in-situ polymerization is shown in Fig 2.5.

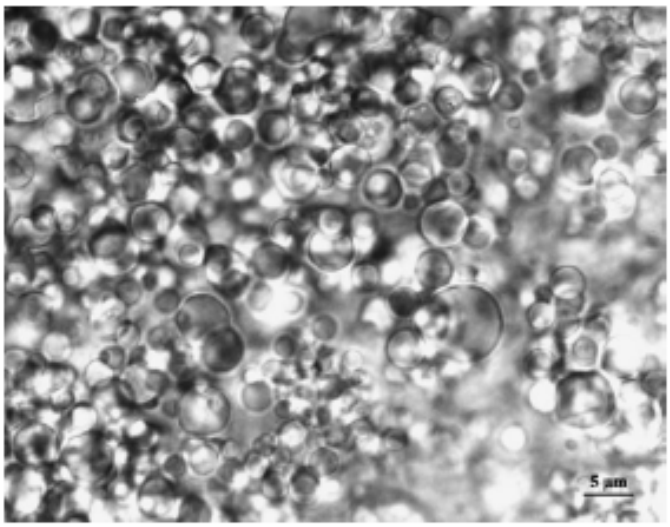


Fig. 2.5. Scanning electron micrograph of silicone microcapsules containing an aqueous solution of self-tanning composition (Courtesy: G.Habar, Microcapsules-Technologies) [12]

2.1.4. Phsico-Chemical Processes

a) Coacervation
b) Encapsulation by Polyelectrolyte Multilayer
c) Polymer Encapsulation by Rapid Expansion of Superficial Fluids
    - Rapid expansion of supercritical solution
    - Gas anti-solvent (GAS) process
    - Particles from a gas-saturated solution (PGSS)
d) Physico-Mechanical Processes
    - Co-Extrusion
    - Spray-Drying
    - Fluidized-Bed Technology
    - Spinning Disk

a) Coacervation

The first systematic approach of phase separation –that is, partial desolvation of a homogeneous polymer solution into polymer-rich phase (coacervate) and the

poor polymer phase (coacervation medium)-was realized by Bungenberg and colleagues. These authors termed such a phase separation phenomenon "coacervation". The term originated from the Latin >*acervus*<, meaning "heap". This was the first reported process to be adapted for industrial production of microcapsules.

Currently, two methods of coacervation are available namely simple and complex processes. The mechanism of microcapsule formation for both processes is identical, except for the way in which the phase separation is carried out. In simple coacervation a desolvation agent is added for phase separation, whereas complex coacervation involves complexation between two oppositely charged polymers.

Complex coacervation; Complex coacervation is carried out by mixing two oppositely charged polymers in a solvent (usually water); the process is shown schematically in Figure 2.6.

The three basic steps in complex coacervation are: i) preparation of the dispersions or emulsion; (ii) encapsulation of the core; and iii) stabilization of the encapsulated particle. First the core material (usually oil) is dispersed into polymer solution (e.g. a cationic aqueous polymer). The second polymer (anionic, water-soluble) solution is then added to the prepared dispersion. Deposition of the shell material onto the core particles occurs when the two polymers form a complex. This process is triggered by the addition of salt or by changing the pH, temperature or by dilution of the medium.

The shell thickness can be obtained as desired by controlled addition of the second polymer. Finally, the prepared microcapsules are stabilized by crosslinking, desolvation or thermal treatment.

Complex coacervation is used to produce microcapsules containing fragrant oils, liquid crystals, flavors, dyes or inks as the core material. Porous microcapsules can also be prepared using this technique. When using this technique, certain conditions must be met to avoid agglomeration of the prepared capsules. A micrograph of microcapsules prepared using the coacervation technique is shown in Fig. 2.7.

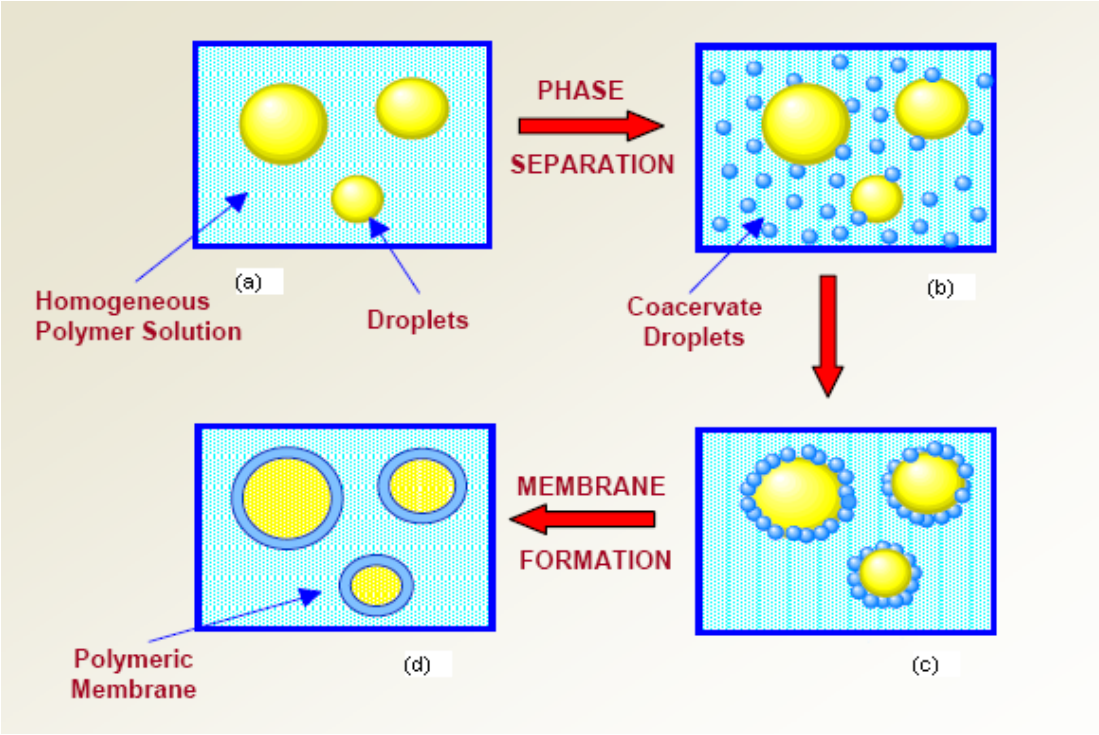


Fig. 2.6: Schematic Representation of The Coacervation Process. (a) Core Material Dispersion in Solution of Shell Polymer; (b) Separation of Coacervate From Solution; (c) Coating of Core Materials by Micro Droplets of Coacervate; (d) Coalescence of Coacervate to Form Continuous Shell Around Core Particles [12].

b) Encapsulation by Polyelectrolyte Multilayer

Layer by layer (L-B-L) electrostatic assembly of electrically charged particles has attracted much attention due to its enormous potential in multilayered thin film preparations with a wide range of electrical, magnetic and optical properties. Polyelectrolyte multilayers are the most widely studied examples of L-B-L assembly, and are prepared by sequentially immersing a substrate in positively, and negatively charged particles such as nanoparticles, ionic dyes and metal ions are used for preparing L-B-L assembly. Core-shell particles with tailored size and properties are prepared using colloidal particle as the material that serves as a template onto which multilayers are fabricated. Hollow capsules of organic, inorganic or hybrid particles can be obtained by dissolving the core material. This technique is both versatile and simple, with the multiplayer film thickness being controlled precisely by varying the total number of layers deposited; in this way the final properties can be tuned.

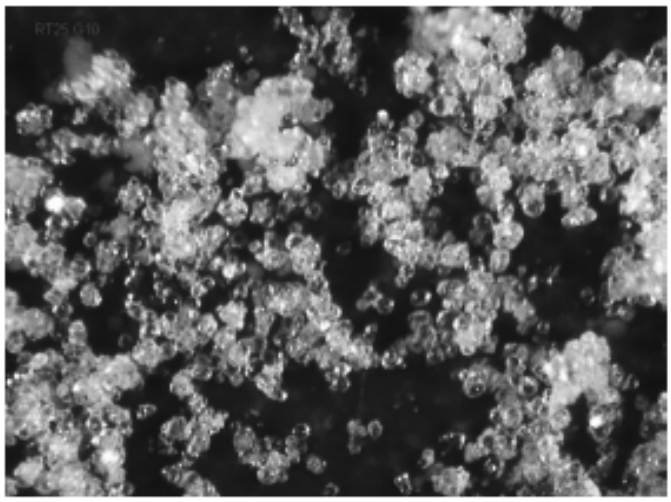


Fig. 2.7: Gelatin Microcapsules Containing a Phase Change Material Prepared by the Coacervation Method. (Courtesy: G.Habar, Microcapsules-Technologies) [12].

c) Polymer Encapsulation by Rapid Expansion of Superficial Fluids

Supercritical fluids are highly compressed gasses that posses several advantageous properties of both liquids and gases. These fluids have attracted much attention in recent years, the most widely used being supercritical CO_2, alkanes (C_2 to C_4), and nitrous oxide (N20). They have low hydrocarbon-like solubility for most solutes and are miscible with common gases such as hydrogen (H_2) and nitrogen (N_2). A small change in temperature or pressure causes a large change in the density of supercritical fluids near critical point – a property which enhances their use in several industrial applications. Supercritical CO_2 is widely used for its low critical temperature value, in addition to its nontoxic, non-flammable properties; it is also readily available, highly pure and cost-effective. It has found applications in encapsulating active ingredients by polymers. Different core materials such as pesticides, pigments, pharmaceutical ingredients, vitamins, flavors, and dyes are encapsulated using this method. A wide variety of shell materials that either dissolve (paraffin wax, acrylates, polyethylene glycol) or do not dissolve (proteins, polysaccharides) in supercritical CO_2 are used for encapsulating core substances. The most widely used methods are as follows:

- Rapid expansion of supercritical solution (RESS)
- Gas anti-solvent (GAS)
- Particles from gas-saturated solution (PGSS)
- Rapid expansion of supercritical solution

In this process supercritical fluid containing the active ingredient and the shell material are maintained at high pressure and then released at atmospheric pressure through a small nozzle. The sudden drop in pressure causes desolvation of the shell material, which is ten deposited around the active ingredient (core) and forms a coating layer. The disadvantage of this process is that both the active ingredient and the shell material must be very soluble in supercritical fluids. In general, very few polymers with low cohesive energy densities (e.g. polydimethyl-siloxanes, polymethacrylates) are soluble in supercritical fluids such as CO_2. The solubility of polymers can be enhanced by using co-solvents. In some cases non-solvents are used; this increases the solubility in supercritical fluids, but the shell materials do not dissolve at atmospheric pressure. A schematic of the microencapsulation process using supercritical CO_2 is shown in Fig. 2.8.

Kiyoshi et al. had very recently carried out microencapsulation of TiO_2 nanoparticles with polymer by RESS using ethanol as a nonsolvent for the polymer shell such as polyethylene glycol (PEG), poly (styrene)-b- (poly (methylmethacrylate)-co-poly(glycidal methacrylate) copolymer (PS-b-co-PGMA) and poly(methyl methacrylate).

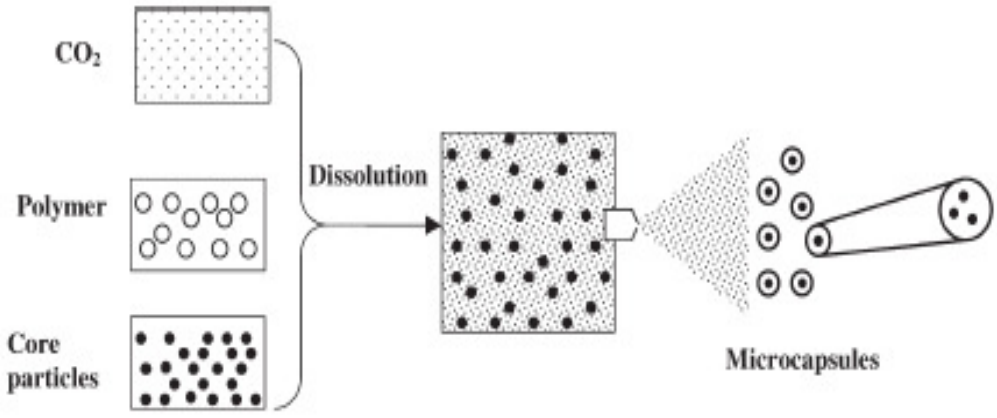


Fig. 2.8: Microencapsulation by Rapid Expansion of Supercritical Solutions (RESS) [12]

GAS anti-solvent (GAS) process is also called supercritical fluid anti-solvent (SAS). Here, supercritical fluid is added to a solution of shell material and the active ingredients and maintained at high pressure. This leads to a volume expansion of the solution that causes super saturation such that precipitation of the solute occurs. Thus, the solute must be soluble in the liquid solvent, but should not dissolve in the mixture of solvent and supercritical fluid. On the other hand, the liquid solvent must

be miscible with the supercritical fluid. This process is unsuitable for the encapsulation of water-soluble ingredients as water has low solubility in supercritical fluids. It is also possible to produce sub micron particles using this method.

Particles from gas-saturated solution (PGSS) process are carried out by mixing core and shell materials in supercritical fluid at high pressure. During this process supercritical fluid penetrates the shell material, causing swelling. When the mixture is heated above the glass transition temperature (T_g), the polymer liquefies. Upon releasing the pressure, the shell material is allowed to deposit onto the active ingredient. In this process, the core and shell materials may not be soluble in the supercritical fluid.

Within the pharmaceutical industry, preformed micro particles are often used for the entrapment of active materials using supercritical fluids under pressure. When the pressure is released, the micro particles shrink and return to their original shape and entrap the ingredients.

d) Physico-Mechanical Processes

The co-extrusion process was developed by Southwest Research Institute in the United States, and has found a number of commercial applications. A dual fluid stream of liquid core and shell materials is pumped through concentric tubes and form droplets under the influence of vibration (Fig. 2.9). The shell is then hardened by chemical crosslinkings, cooling, or solvent evaporation. Different types of extrusion nozzles have been developed in order to optimize the process.

Microencapsulation by spray drying is a low-cost commercial process, which is mostly used for encapsulation of fragrances, oils and flavors. Core particles are dispersed in a polymer solution and sprayed into a hot chamber (Fig. 2.10). The shell material solidifies onto the core particles as the solvent evaporates such that the microcapsules obtained are of poly-nuclear or matrix type. Very often the encapsulated particles are aggregated and the use of large amounts of the core material can lead to uncoated particles. However, higher loadings of core particles of up to 50-60% have been reported. Water-soluble polymers are mainly used as shell materials because solvent-borne systems produce unpleasant odors and environmental problems.

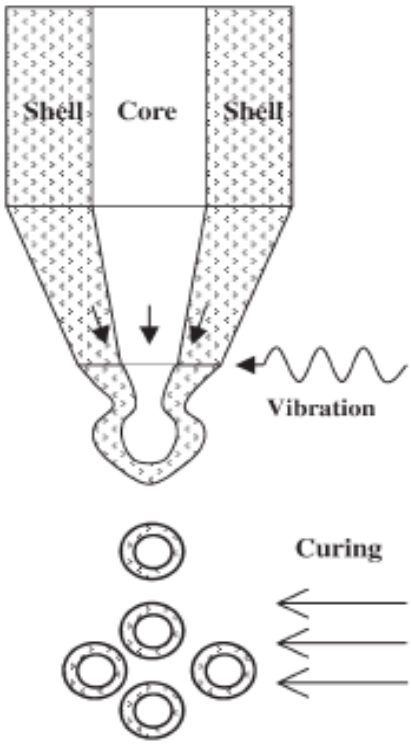


Fig. 2.9: Schematic Presentation of The Coextrusion Process [12]

Fluidized-Bed Technology; with the high demand for encapsulated materials in the global market, fluid-bed coaters have become more popular. They are used for encapsulating solid or porous particles with optimal heat exchange. The liquid coating is sprayed onto the particles and the rapid evaporation helps in the formation of an outer layer on the particles. The thickness and formulations of the coating can be obtained as desired. Different types of fluid-bed coaters include top spray, bottom spray, and tangential spray (Fig 2.10).

- In the top spray system the coating material is sprayed downwards on to the fluid bed such that as the solid or porous particles move to the coating region they become encapsulated. Increased encapsulation efficiency and the prevention of cluster formation are achieved by opposing flows of the coating materials and the particles. Dripping of the coated particles depends on the formulation of the coating material. Top spray fluid-bed coaters produce higher yields of encapsulated particles than either bottom or tangential sprays.

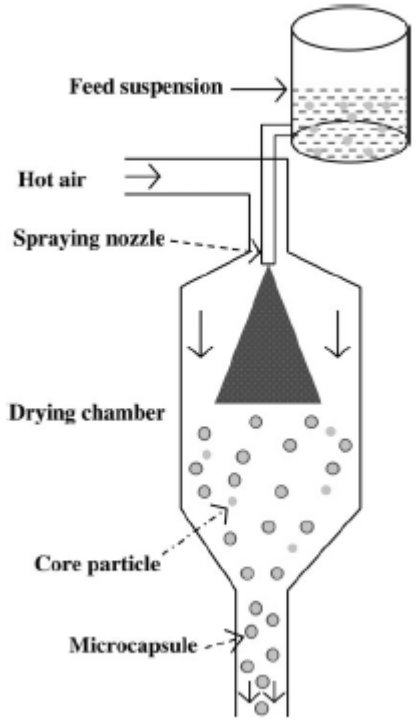


Fig. 2.10: Schematic Illustrating The Process of Microencapsulation by Spray-drying [12].

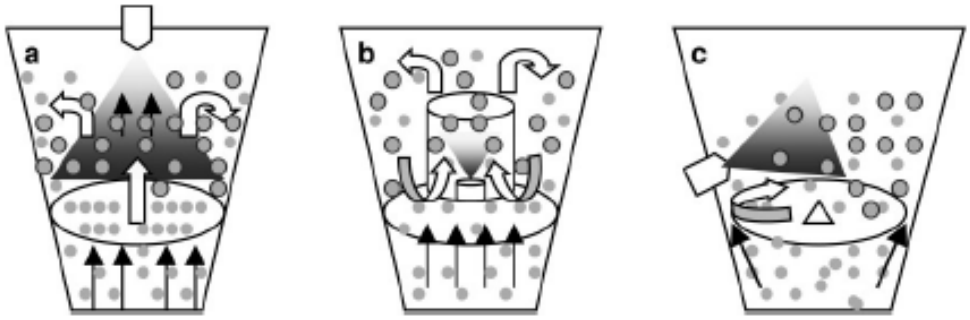


Fig. 2.11. Schematics of fluid-bed coaters. (a) Top spray; (b) Bottom spray; (c) Tangential Spray [12].

- Prof.D.E also knows the bottom spray as “Wurster’s coater” in recognition of its development. This technique uses a coating chamber that has a cylindrical nozzle and a perforated bottom plate. The cylindrical nozzle is used for spraying the coating material. As the particles move upwards through the perforated bottom plate and pass the nozzle area, the coating material encapsulates them. The coating material adheres to the particle surface by evaporation of the solvent or cooling of encapsulated particle. This process is continued until the desired thickness and weight is obtained. Although it is a time-consuming process, the multiplayer coating procedure helps in reducing particle defects (Fig. 2.11).

- The tangential spray consists of a rotating disc at the bottom of the coating chamber, with the same diameter as the chamber. During the process the disc is raised to create a gap between the edge of the chamber and the disc. The tangential nozzle is placed above the rotating disc through which the coating material is released. The particles move through the gap into the spraying zone and are encapsulated. As they travel a minimum distance there is a higher yield of encapsulated particles.

Spinning disk, the microencapsulation of suspended core materials using a rotating disc was first developed by Prof. R.E. Sparks in 1987. A schematic diagram of the process is shown in Fig 2.12. Suspensions of core particles in liquid shell material are poured into a rotating disc and, due to the spinning action of disc; the core particles become coated with the shell material. The coated particles, along with the excess shell material are solidified by external means (usually cooling). This technology is rapid, cost-effective, and relatively simple and has high production efficiencies. For optimum encapsulation, spherical core particles with diameters of ~100 to 150μm and rapidly cooling shell materials are required.

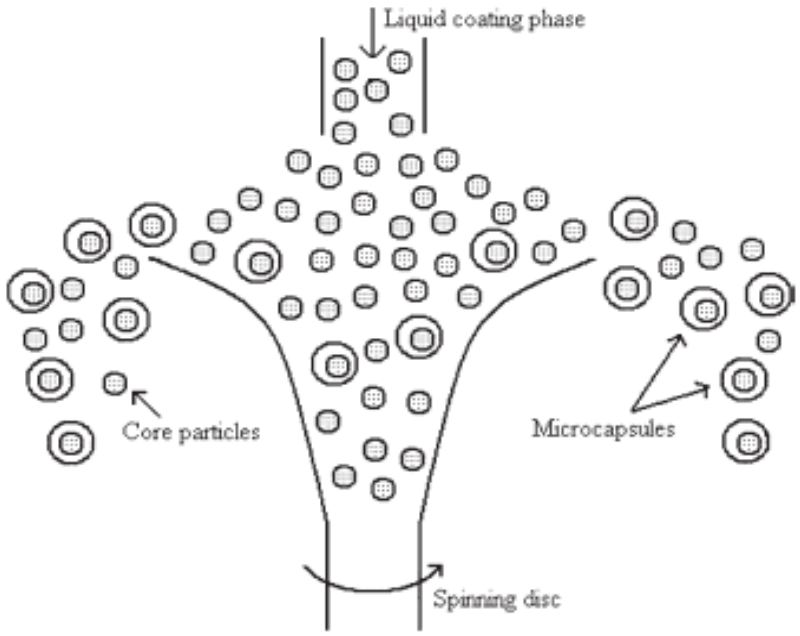


Fig. 2.12: Schematic Representation of Microcapsule Formation by Spinning Disk [12].

Although a variety of alternative microencapsulation techniques are available (for details of sol-gel techniques), no single method is suitable for encapsulating different types of core material. Ultimately, the best method will be depend upon the type of core material, the required particle size, the permeability of the shell wall, and the

different properties of the microcapsule, and consequently the process must be custom-tailored in order to provide a satisfactory outcome. An overview of the size of microcapsules obtained by different techniques is provided in Table 2.4.

2.2. Enhancing Coating Functionalities with Microcapsules

Microcapsules can be used in a wide variety of applications [14], since the versatility of microencapsulation technologies offers unlimited combinations of core and shell materials for their production. To date, few investigations have been made into possible applications of microcapsules in functional coating developments. Microcapsules are applied onto substrate in various ways. For example, they may be sprayed over an existing coating layer, perhaps to provide immediate release of lubricants or perfumes. The most two common process of applying immediate microcapsules in coatings are either to incorporate them into coating formulations or by their electrolytic co-deposition with metal ions (Fig. 2.13)

Table 2.4: Microencapsulation Processes With Their Relative Particle Size Ranges [12].

Microencapsulation process	Particle size (μm)
Extrusion	250-2.500
Spray-drying	5-5.000
Fluid bed coating	20-1500
Rotating disk	5-1500
Coacervation	2-1200
Solvent evaporation	0.5-1000
Phase separation	0.5-1000
In-situ polymerization	0.5-1100
Interfacial polymerization	0.5-1000
Mini-emulsion	0.1-0.5
Sol-gel encapsulation	2-20
Layer-by-layer (LBL) assembly	0.02-20

The mixing of microcapsules with coating binders requires compatibility of the shell material with the binder. Generally, microcapsules are used in coatings for controlled-release applications, but microcapsules containing active ingredients such as biocides can also be trapped inside a coating matrix that will release the contents slowly over time. Another interesting example is to use microcapsules in the development of self-healing coatings. For this, microcapsules containing monomer,

cross-linker or catalysts are incorporated into a coating matrix such that, when a coating ruptures, the microcapsules along the rupture break open and release their contents. Subsequently, the monomer polymerizes, cross-links, and fills the damage, thereby preventing further propagation. An innovative example is the use of microencapsulated phase-change material (PCM) particles in interior coatings for buildings. During the day, as the temperature rises, the core material melts and stores heat. During the night when the temperature falls, the heat stored inside of the capsules is released, thereby reducing energy needs. Clearly, for heat management to be effective, the correct quantities of microcapsules must be used in the preparation of such coatings. Other applications include microencapsulated dyes used to formulate color coatings, and foaming agents (e.g. sodium bicarbonate), which can be microencapsulated to generate foams during curing processes. Microcapsules containing perfumes, insecticides, chemicals, and heat or pressure-sensitive dyes can also be used for functional coating preparations. The use of polymers with different T_g values can be used to create microcapsules that can be added to coating in order to produced specialized functions, for example vibration damping. Finally, microcapsules containing nanoparticles may be used in the design of functional surfaces with improved physical, optical, mechanical, electrical, or chemical properties.

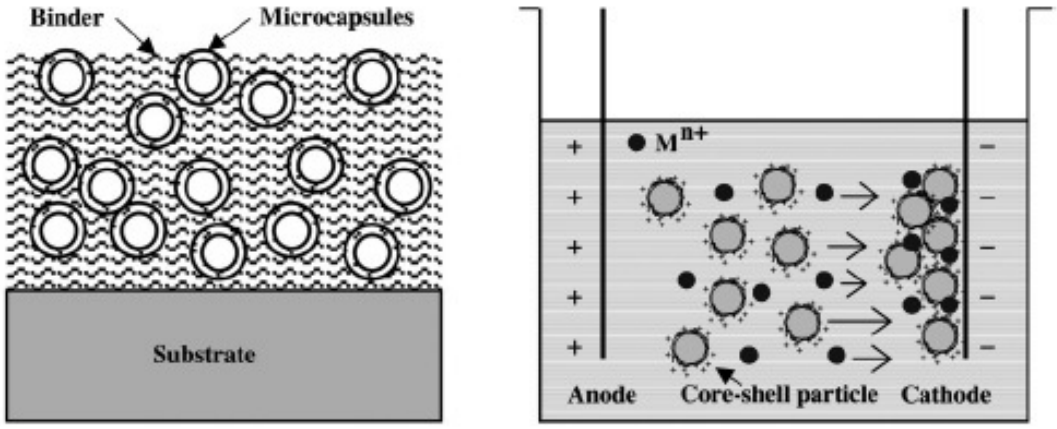


Fig. 2.13: Left Schematic Diagram Showing Pathways For Microcapsules Incorporating into Coating; Blending of Microcapsules with Binders. Right Schematic Diagram Showing The Electrolytic Co-deposition of Microcapsules with Metallic Ions [12]

2.3. Other Concepts For Intelligent/ Smart Textiles

Beside microcapsules, other concepts were developed to fulfill needs for intelligent textiles.

An alternative approach to confer better insulation properties to textiles is the use of shape-memory effects. The incorporation of shape-memory material can be done with either shape-memory polymers or shape-memory alloys. Shape-memory polymers were originally designed from blends of elastomers and glassy thermoplastics, but recently developed versions are types of polyurethanes. Polyurethane films, for example, can be incorporated between adjacent layers of clothing. When the temperature of the outer layer has fallen sufficiently, the polyurethane film responds so that an air gap between the layers of clothing becomes wider. Shape-memory alloys, such as nickel/titanium, posses different properties below and above temperature at which it is activated. The temperature of activation can be chosen by altering the ratio of nickel titanium in the alloy [11].

Another technology that leads to a variety of processes to modify fiber or textile materials to fulfill highly desirable requirements is low plasma technology. There are two, equally important forms of low plasma technology; glow-discharge technology under reduced pressure and barrier discharge, and corona treatment under atmospheric pressure. In both cases, active particles such as radicals, ions, electrons, and photons are generated which further provoke general reactions with the textile surface. Reactions to be achieved are oxidation of the surface, generation of radicals, and edging of the surface; when using special gases (i.e. reduced pressure treatments) a plasma-induced deposition polymerization may occur. Fır the treatment of textiles this means that hydrophilisation as well as hyrophobisation may be achieved; moreover, both surface chemistry and surface topography may be influenced to result in improved adhesion or repellency properties as well as in the confinement of functional groups to the surface [16].

Till now, plasma treatments were shown to be suitable for

- Desizing of cotton fabrics;
- Successful shrink-resistance treatment for wool, with a simultaneously positive effect on dyeing and printing;

- Modifying man-made fibers with diffusion barrier layers on their surface in order to improve their stability.
- Hyrdophobisation treatment of cotton (so-called Lotus effect [17])

The morphology of wool is highly complex; yet, the surface is highly hydrophobic. Plasma treatment of wool has thus different effects on the surface. Chemical and physical surface modifications due to plasma treatment result in decreased shrinkage behavior of wool; the felting density decreases from 0.2 g/cm^3 to less than 0.1 g/cm^3. However, with the respect to shrink-resist treatment, this effect is too small as compared with the state of the art processes, i.e. the chlorine/ Hercosett treatment. Therefore, additional resin coverage of the fiber surface is required. This leads to smooth surface and area shrinkage in the range of design, i.e. a little more than 1%. Additional advantages of plasma treatment on wool are in particular; the increasing dyeing kinetics, an enhanced depth of shade, and improved bath exhaustion. A surface treating barrier discharge machine (i.e. corona treatment on atmospheric pressure) on a pilot plant scale is currently in the use in the industry. [18]. Moreover, interesting dyeing effects can be obtained with wool treated with different gas plasma. A treatment with SO_2-plasma is used to incorporate sulfonic groups into the woolen surface. As sulphonic groups rather have retarding effect on dyeing, the hue obtained when colouring this fiber is less intensive as those of amino-wool. Yet, the dyeing of fabrics has to take place rather soon after plasma treatment [18].

Moreover, plasma treatment of synthetic fibers can modify the surface by allowing a deposition polymerization, depending on the special gases used. Polypropylene surfaces, for example, afford a permanent hydro-philisation when using maleic acid anhydride as an assisting agent (i.e.so-called plasma-induced grafting) and a glow-discharge treatment. When polyethylenterephtalate fibers are used as an enforcing material for polyethylene matrix, an ethylene plasma treatment can increase impressively the adhesion strength of the composite material. With a mixture of ethylene and hexafluoroethane as plasma gas, alcohol repellency is obtained. Furthermore, polyaramid fibers - so called high performance fibers – can be treated with hexafluoroethane / hydrogen plasma in order to improve their resistance to hydrolysis. For this purpose, a diffusion barrier layer is applied to the surface, which also results in high alcohol repellency values, and gives much better resistance to 85% sulphuric acid treatment than conventional fluorocarbon finishing. [16].

Fiber surfaces modified with plasma treatment are also expected to show improved dust and dirt repellent properties, and hence fibers should also be repellent to bacteria and fungi.

Further example of achieving water repellency using plasma is the plasma polymerization of ethen on cotton fibers. The method is said to be an ecological interesting alternative to other hydrophobic finishing [18].

2.4. Important Parameters Which Play Active Roll in Microencapsulation Process

There are a lot of parameters, which directly affect the Microencapsulation Process such as:

- Polymer type used in microencapsulation process
  In this thesis, mainly Urea-Formaldehyde (UF), Melamine-Formaldehyde (MF) microencapsulation processes and conditions were examined.
- Microencapsulation materials and conditions;
- Stirring rate, stirring time,
- Ph change, viscosity of the core material,
- Emulsifier type,
- Immersion rate (dropping speed of the wall polymer).

2.4.1. Urea-Formaldehyde (UF) Microcapsules

In the study of Soo-Jin Park, et al.[19], urea-formaldehyde microcapsules were prepared by in situ interfacial polymerization to lemon oil as the core material using four kinds of emulsifier, gelatin, span 80, polyvinyl alcohol, and sodium dodecyl sulfate. Urea-formaldehyde types were investigated for their effects on thermal properties, mean particle size, and size distributions. Thermal properties were studied using a dynamic DSC and TGA analysis. The morphology and particle distributions of microcapsules were determined using an image analyzer. As experimental results, the diameters and distribution ranges of the microcapsules were decreased with increasing stirring rate and stirring time. In the presence of up to 5g of emulsifier in 100ml of deonized water, the mean diameter decreased, and then it increased as the emulsifier increased, resulting from increasing viscosity. The mean size of microcapsules was related to the viscosity and reunification of core materials. That

is, the mean size increased up to 22.8cP due to increased viscosity. But, at 30cP, the mean size of the microcapsules decreased, as a consequence of the interruption of the reunion of core materials by the high viscosity of the core materials.

The polymeric wall of microcapsule commonly has a permeable part with high porosity or a less permeable matrix part with low porosity. The porosity of the microcapsule wall determines the release behavior of core materials and microcapsule morphology. For urea microcapsules it is possible to vary the degree of crystallinity of the membrane wall, for the same polymer, through the choice of preparation conditions. But the characteristics of urea microcapsules containing functional core substances, such as fragrance, have rarely been studied with regard to

a. Structure
b. Size distribution
c. Thermal properties
d. Emulsifier
e. Viscosity as affected by the use of formaldehyde in emulsion polymerization.

The size of microcapsules is very dependent on the physical factors, such as the rate of shear, the phase viscosity, and the concentration of stabilizers, as well as, the design of the stirrer and vessel. Hong and Park proposed investigation of the effects of mechanical and chemical parameters on the characteristics of polymeric microcapsules.

Liquid cores and solid shells, lemon oil, and urea-formaldehyde used in microencapsulation may be prepared by a number of methods. The in situ interfacial polymerization of microencapsulation in this case relies on monomers in the oil phase reacting at the o/w interface with monomers from the aqueous phase. In this process, the pre-polymers are incorporated only into the oil phase and they are polymerized interfacially by increasing temperature.

Soo-Jin Park studied, urea-formaldehyde microcapsules containing fragrant oil which were prepared by in situ interfacial polymerization. The objective of this study was to investigate the interfacial polymerization of microcapsules measured by surface functionality, thermal properties, and morphology. Key process parameters, stirring

time and speed, emulsifier sort and content, and the viscosity of the core material, affecting the formation and the morphology of microcapsules, were also identified.

Urea and 37% formaldehydes, used as wall materials in Soo-Jin Park study, were obtained from Junsei Chem. of Japan without any further purification. The emulsifiers used were gelatin, Span 80, polyvinyl alcohol (PVA), and sodium dodecyl sulfate (SDS) to compare the morphology and particle distribution size of microcapsules from different emulsifiers and find the most proper emulsifier under urea-formaldehyde microcapsule preparation conditions.

Preparation of Microcapsules: Urea (4M) and 37% formaldehyde (10M) in 100 ml of distilled water were adjusted to a pH of about 8 to 8.5 with triethanolamine and stirred at 70^0C for 1 h. Urea-formaldehyde microcapsules were made from a preformed polymer (pre-polymer) by stirring with 6 ml of lemon oil and emulsifiers including gelatin, Span 80, PVA, and SDS at 20^0C for 30 min with maintaining the pH at about 3 with 10% citric acid aqueous solution. Microcapsules were prepared according to the stirring time, the stirring rate, the sort of emulsifier, the emulsifier content, and the viscosity of the core materials.

Structure of Microcapsules: Fig 2.14 presents the suggested reaction mechanism of urea-formaldehyde pre-polymer. The new CN bond and OH group appear in the urea-formaldehyde pre-polymer. Fig. 2.15 shows the FT-IR spectra of urea-formaldehyde microcapsule containing lemon oil to confirm the preparation of urea-formaldehyde microcapsule.

According to FT-IR spectra, it was shown that three peaks of a N-H stretching vibration at 1571 cm^{-1} , a C=0 stretching vibration at 1650 cm^{-1}, and a C-H stretching vibration at 1460 cm^{-1} were observed. C-N stretching vibrations were shown at 1286 and 1142 cm^{-1}. The O-H peak was shown as a broad absorption peak at 3500- 3200 cm^{-1}. So it was found that urea-formaldehyde pre-polymer was formed, while the specific absorption bands of lemon oil were not observed in the microcapsule due to the sealing of lemon in the microcapsule.

$$\underset{\text{Urea}}{CO(NH_2)_2} + \underset{\text{formaldehyde}}{COH_2} \longrightarrow \underset{\text{urea-formaldehyde pre-polymer}}{H_2NCONHC(OH)H_2} \qquad (2.3)$$

Fig 2.14: Reaction Mechanism for Urea and Formaldehyde [19]

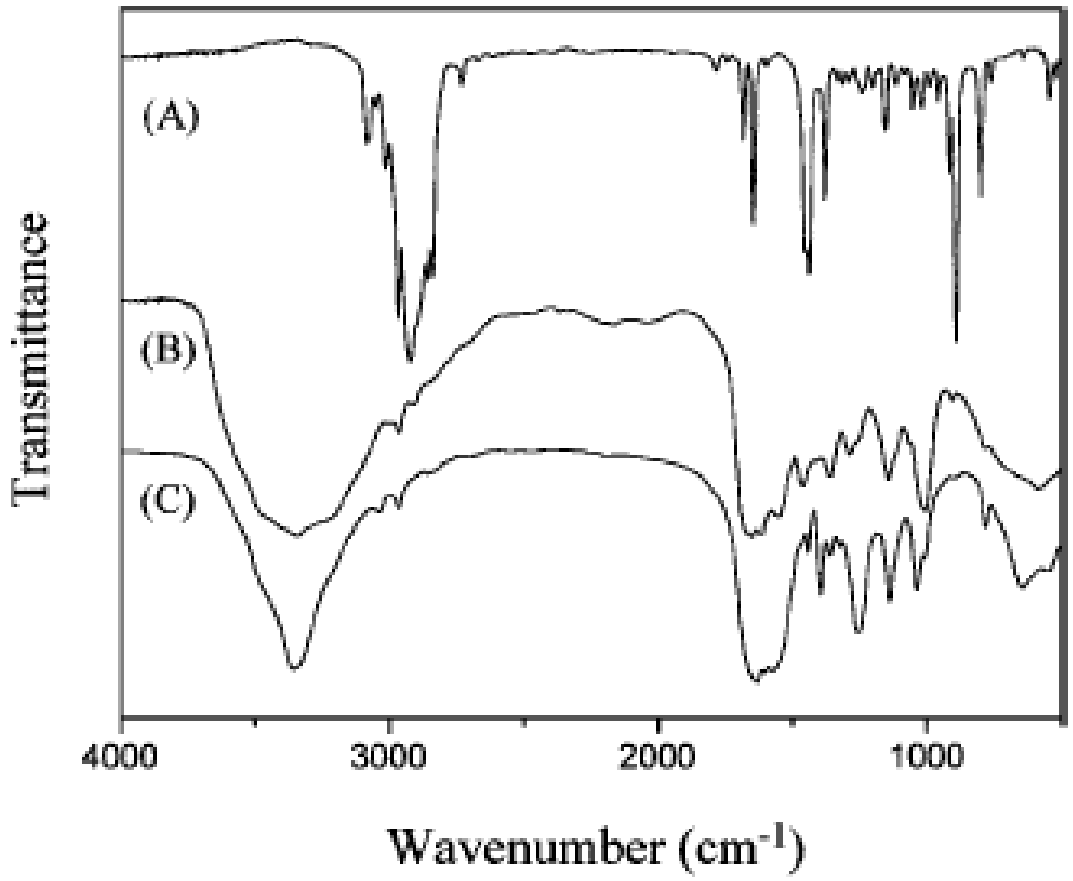


Fig 2.15: IR Spectra of Urea-Formaldehyde Resin Microcapsules: (A) Lemon Oil, (B) Pre-polymer, and (C) Microcapsule [19].

Thermal properties: Fig. 2.16 shows the results of dynamic DSC curves for the melting of lemon oil, pre-polymer, and the prepared urea-formaldehyde microcapsules containing lemon oil. The thermo-grams of lemon oil, pre-polymer, and microcapsules showed endothermic transitions at 180^0C for the melting point in lemon oil, 250^0C in pre-polymer, and 180 and 250^0C in the microcapsule, respectively. From the DSC results, it was noted that microcapsule was composed of two materials. Eventually, lemon oil existed in the urea-formaldehyde pre-polymer.

The TGA thermo-grams of urea-formaldehyde pre-polymer and microcapsules containing lemon oil are shown in Fig 2.17. It was shown that the decomposition temperature is connected to the melting temperature.

The weight loss for the pre-polymer and urea-formaldehyde microcapsules started at the melting point. Microcapsules show an initial weight loss of about 5% from 50 to about 250^0C, but pre-polymer did not show weight loss up to 250^0C,

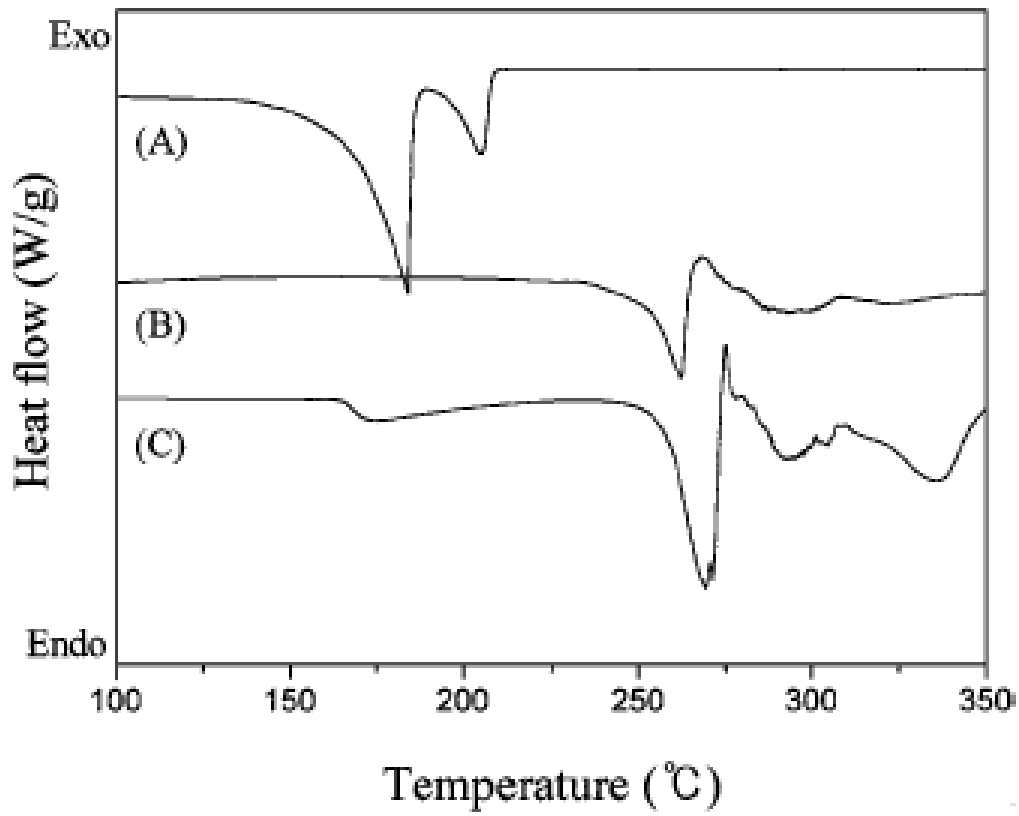


Fig. 2.16: DSC Thermo-grams of Urea-formaldehyde- Based Microcapsules: (A) Lemon oil, (B) Pre-polymer, and (C) Microcapsule [19].

a subsequent weight loss of up to 80 and 95% occurred for the pre-polymer and microcapsule, respectively. There is about a 15% residual weight difference by temperature change of the pre-polymer and microcapsule containing lemon oil. From TGA, the microcapsules contain about 15% lemon oil.

Particle Size Distribution According to Stirring Conditions: Fig. 2.18 shows the particle size distribution of the prepared urea-formaldehyde microcapsules containing lemon oil at the different stirring rates in the emulsion. i.e. 40, 120, 240, and 360 min. Especially, the rate of those over 200 μm in size is about 17% for 40 min due to insufficient time to be separated by the stirrer in the emulsion (Fig 2.16) The image photographs of surface morphologies with different stirring times are shown in Fig. 2.20. The sizes of the microcapsules are small and the number of the microcapsules with increasing time. The particle distribution becomes narrower and the particles become smaller due to particles being separated for longer periods of time by the stirrer in the emulsion phase, with increasing time. As expected, the increase of stirring time plays an important part in producing more microcapsules and smaller sizes.

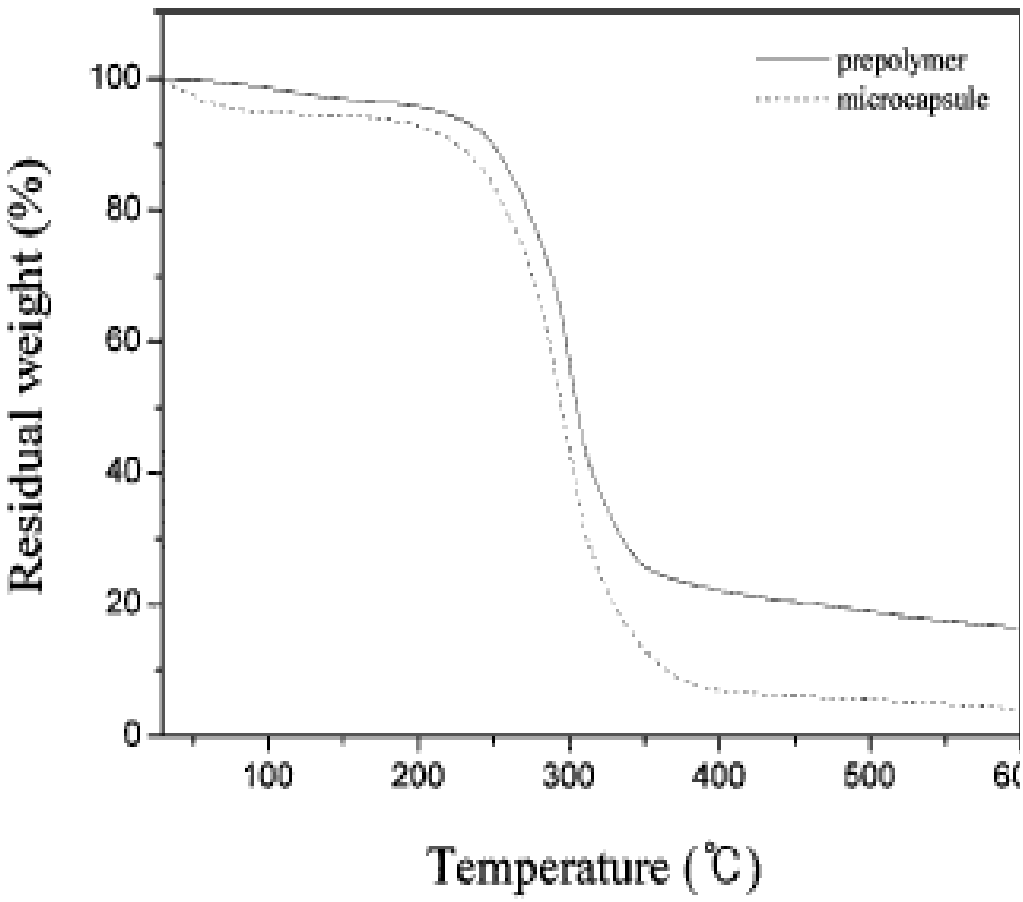


Fig. 2.17: TGA Thermo-grams of Urea-Formaldehyde Based Microcapsules [43].

Particle Size Distribution According to Emulsifiers: Fig. 2.21 shows the particle size distribution of microcapsules prepared using different emulsifiers, i.e. gelatin, Span 80, PVA, and SDS. The particle size distribution is concentrated at 40-60 μm due to dispersed particles in emulsion.

Fig. 2.22 shows the microcapsules prepared from different emulsifiers using an image analyzer. In PVA, the particle size is small and the production rate is low. In gelatin, the particle size is varied, and in Span 80, the particle morphology is ugly. However, in the case of SDS as repulsive force agent, the particle distribution is appropriate and the production rate is excellent. In Park, Shin and Lee study, SDS seems to be adequate for the preparation of urea-formaldehyde microcapsules with regard to the morphology of the particle and the particle size distribution.

Fig 2.23, presents the particle distribution of microcapsules at different emulsifier contents, i.e. 1, 2.5, 5, and 10%. As seen in Fig 2.23, the total graph is shifted to the side of small particle size of the emulsifier and water and interaction of micelles with increasing emulsifier content. At 10% emulsifier content, the particle distribution of

microcapsules becomes larger due to adhesion of the particles by increasing viscosity according to the increase of concentration in solution.

Particle Size Distribution According to Core Material Viscosities: Particle distributions of microcapsules prepared with different core material viscosities, i.e., 0.82, 22.8, and 30 cPSs, are shown in Fig. 2.24. As shown in Fig. 2.24, the particle distribution becomes larger up to 22.8cP, but at 30cP, the particle distribution becomes smaller. Therefore, the mean size is increased with increasing viscosity due to increasing interfacial tension at high viscosity. As mentioned above, the mean size of a microcapsule is decreased in 30cP. This is a consequence of the interruption of the interfacial reunion of core materials by the high viscosity of the core materials.

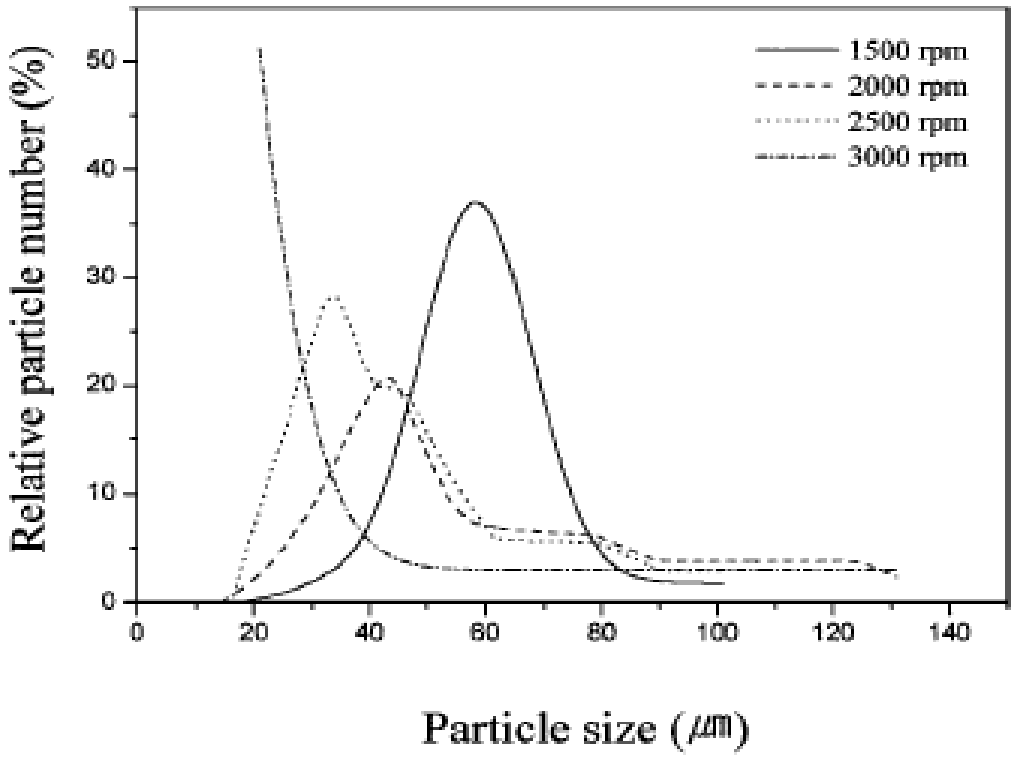


Fig. 2.18: Particle Size Distribution of Microcapsules Prepared at Different Stirring Rates [19].

In the study of Park, Shin and Lee, urea-formaldehyde microcapsules containing lemon oil were prepared by in-situ interfacial polymerization. The particle size and distribution under different experimental conditions were measured to investigate interfacial polymerization using FT-IR, DSC, TGA, and image analyzer, and a viscometer. The prepared microcapsules contained 15% lemon oil, derived from the residual weight difference of the microcapsule and pre-polymer. It was found that the particle sizes of the microcapsules were largely dependent on the stirring rate and

stirring time. The SDS emulsifier seemed to be adequate for the preparation of urea-formaldehyde microcapsules, resulting in the development of the morphology and particle size distribution by means of repulsive force. Also, it was found that the particle sizes of urea-formaldehyde microcapsules containing lemon oil were the smallest at 5% emulsifier content.

In according to the study of K.Hong, S.Park [20], the characteristic of microcapsule wall depends on the chemical and physical processing condition such as the type and concentration of the constituents as well as the microencapsulation methods. If other processing conditions are the same, the characteristics of the microcapsules depend mainly on the types of wall-forming materials.

A. Walter, H.Rehage, H. Leonhard [21] reported that microcapsules can show a broad range of different membrane features, ranging from purely viscous to elastic properties. Available methods to measure these phenomena are membrane aspiration, capsule- sequeezing techniques, and the determination of capsule orientation of deformation in shear flow. Another experimental technique consists of observing the particle in a spinning-drop tensiometer. Additional results can be obtained by measuring rheological properties of the flat membranes using an interfacial rheometer. Each of these measurements gives complementary findings, but in order to get more comprehensive information on the constitutive law of the cross-linked membranes, one has to combine several experimental techniques.

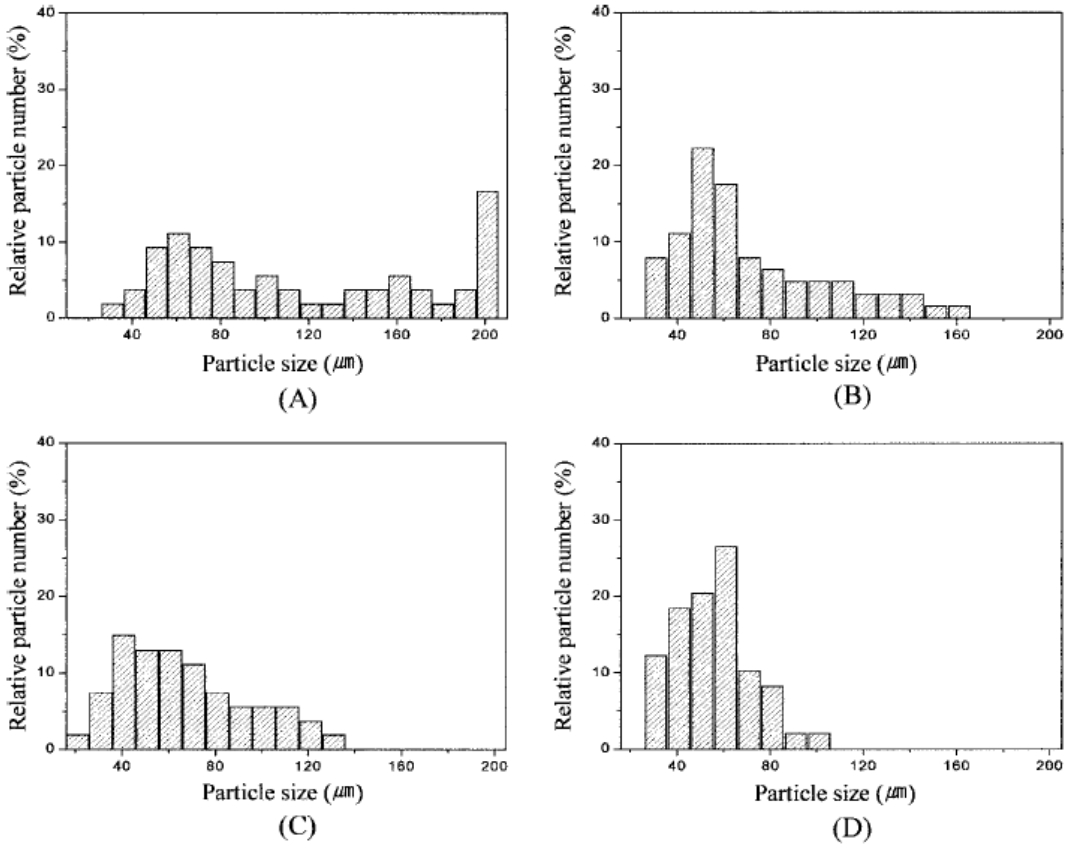


Fig. 2.19: Particle Size Distribution of Microcapsules Prepared for Stirring Times: (A) 40, (B) 120, (C) 240, and (D) 360 min. [19]

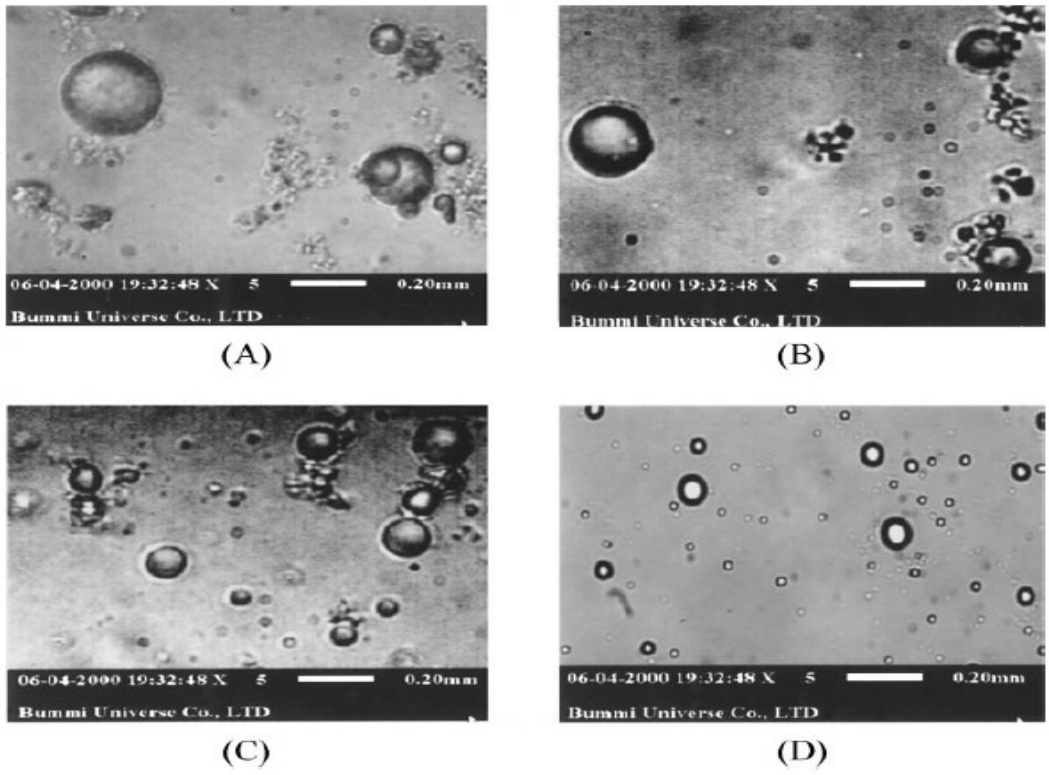


Fig. 2.20: Image Analysis of Microcapsules Prepared at Different Stirring Rates: (A) 1500, (B) 2000, (C) 2500, and (D) 3000 rpm. [19]

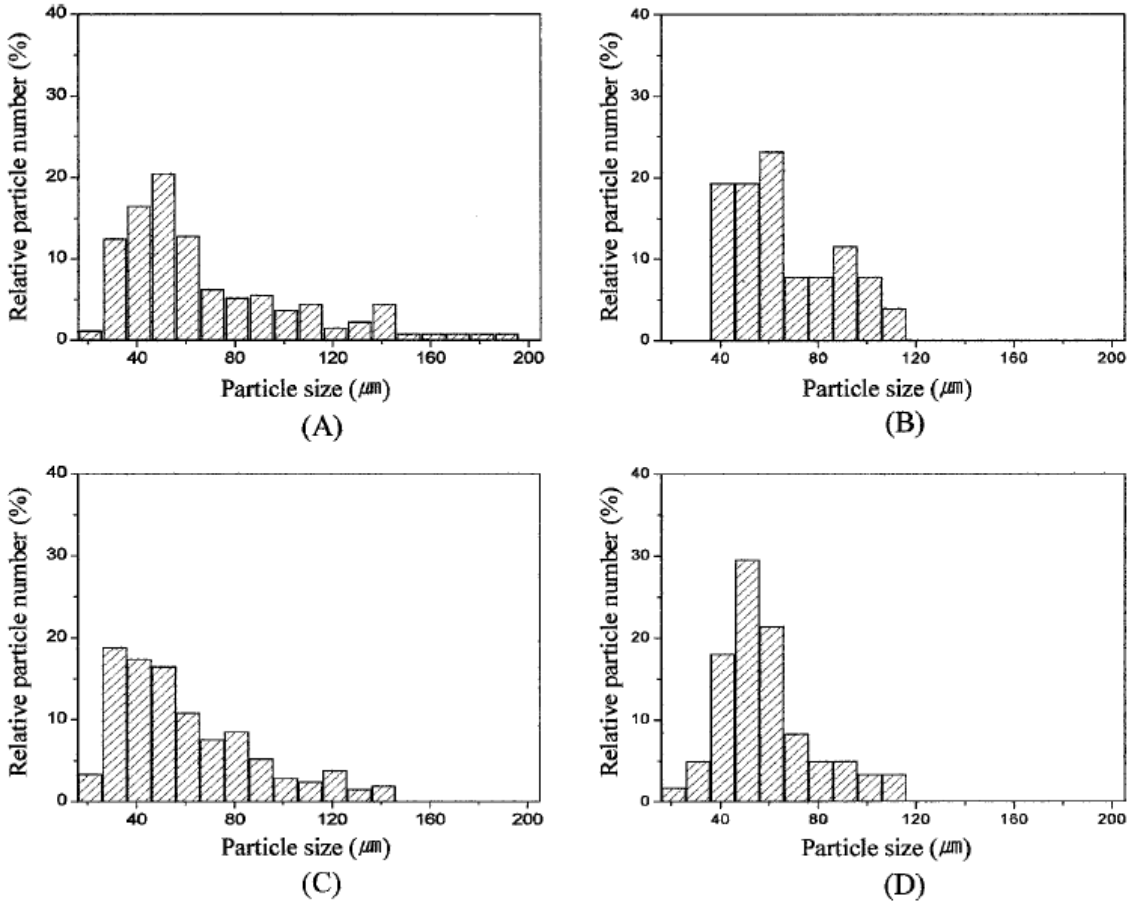


Fig. 2.21: Particle Size Distribution of Microcapsules Prepared with Different Emulsifiers: (A) Gelatin, (B) Span 80, (C) PVA, and (D) SDS [19].

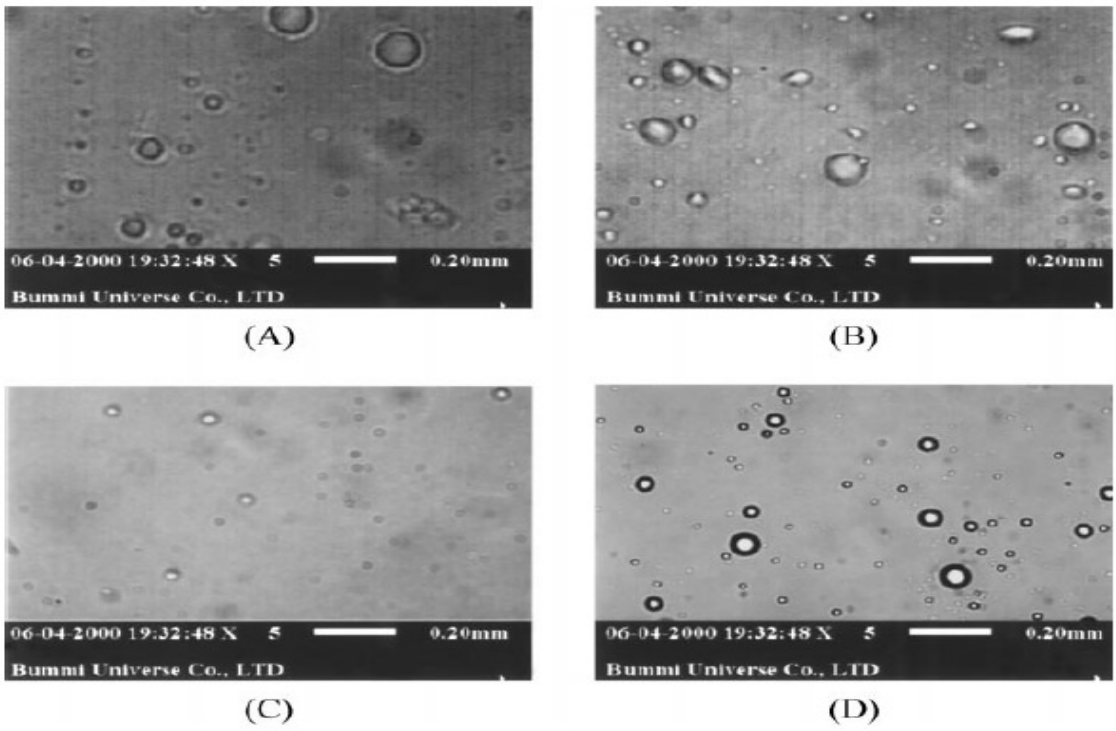


Fig. 2.22: Image Analysis of Microcapsules Prepared with Different Emulsifiers: (A) Gelatin, (B) Span 80, (C) PVA, and (D) SDS [19].

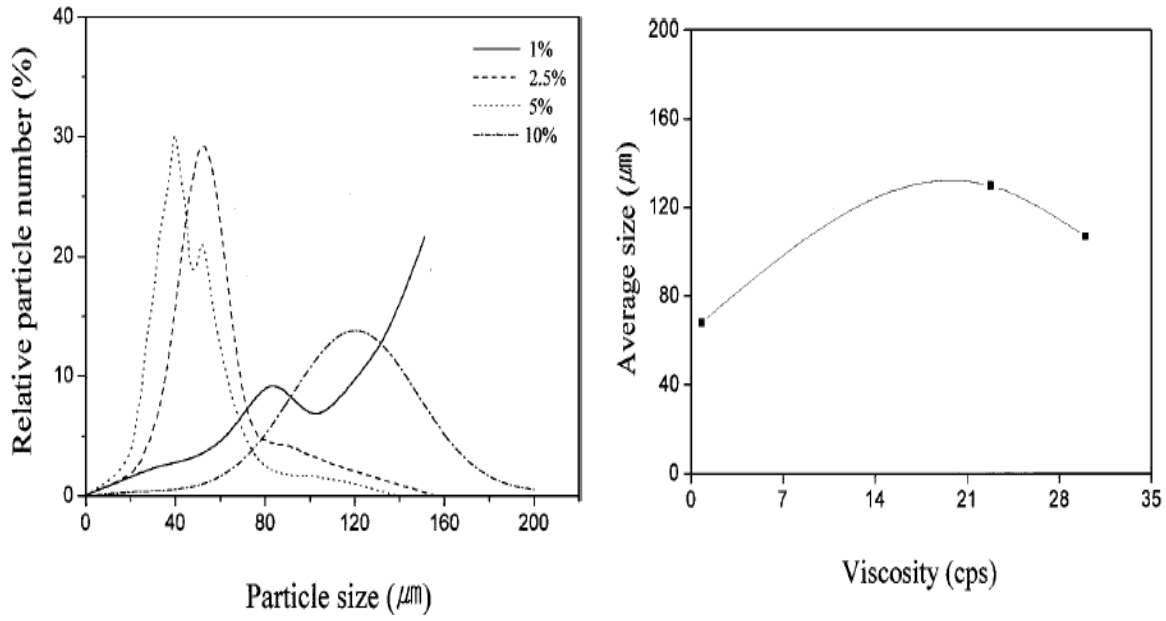


Fig. 2.23: Particle Size Distribution of Microcapsules Prepared with Different Emulsifier Contents. The Right Figure Illustrates The Mean Size of Microcapsules Prepared with Different Viscosities [19].

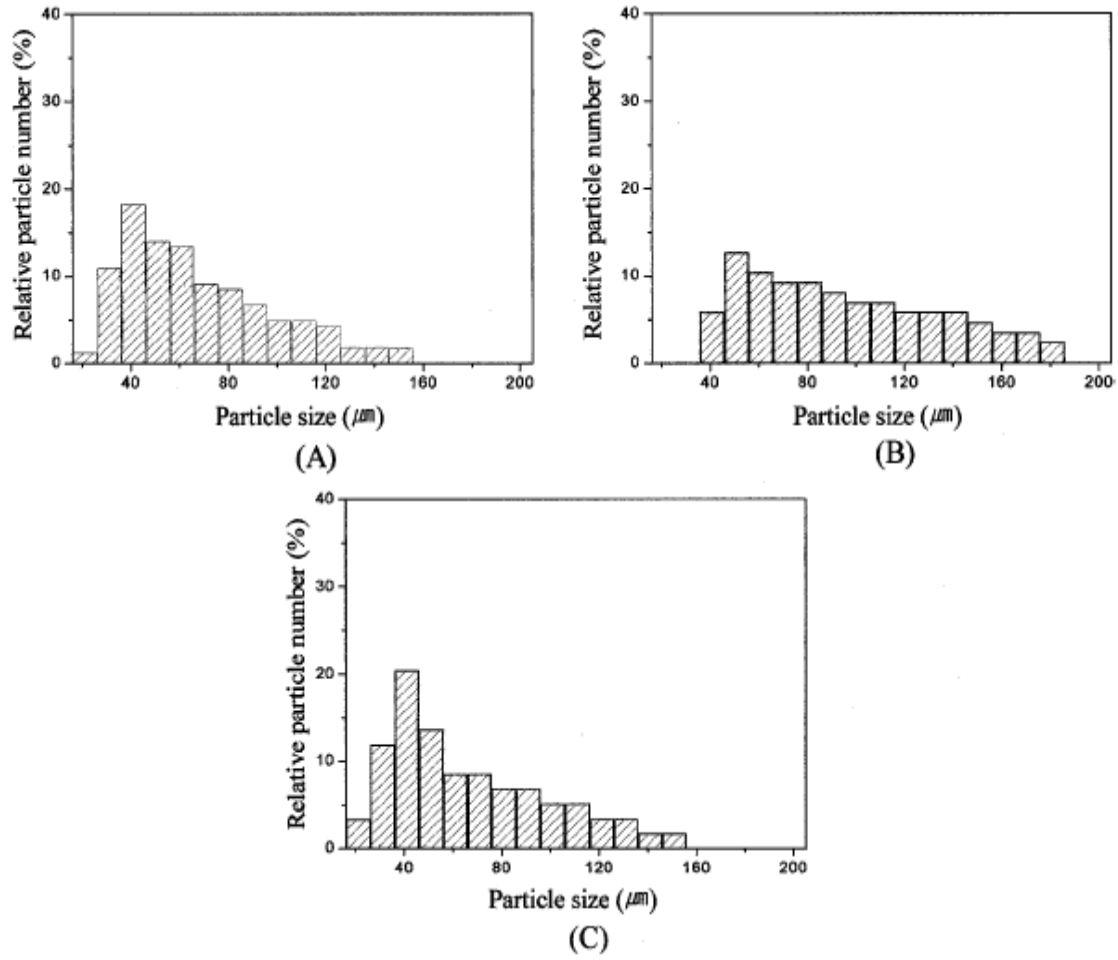


Fig.2.24: Particle Size Distribution of Microcapsules Prepared with Different Viscosities: (A) 0.82, (B) 22.8, and (C) 30cP [19].

2.4.2. Melamine-Formaldehyde (MF) Microcapsules

H.Y.Lee, et al. [22] used melamine-formaldehyde (MF) instead of urea-formaldehyde in their research. And they concentrated on formaldehyde/ melamine (F/M) molar ratio and made lots of measurement in this respect. Most capsule wall materials are organic polymers, such as gelatin, urea-formaldehyde (U-F), polyurethane and melamine-formaldehyde (M-F), but fats and waxes are also used (Kasai and Koishi 1977, Scher 1983). In their study, the in situ polymerization method using M-F was used for the encapsulation of fragrant oil. With in situ polymerization, no reactive materials are added to the core material. Polymerization occurs exclusively in the continuous phase and on the continuous phase side of the interface formed by the dispersed core material and continuous phase. As shell materials, melamine and formalin (37% formaldehyde solution), sodium lauryl sulphate (SLS) and Tween 20 were used as stabilizers and/ or surfactants. For pH control, sodium hydroxides (NaOH) and citric acid 0.5 N aqueous solution were used. DDI (double distilled and deionized) water was used throughout.

Preparation of M-F pre-polymer: A calculated amount of melamine and formaldehyde was injected in 500 ml 3-neck rounded flask equipped with mechanical stirrer and condenser. The reaction mixture was heated to 85˚C and the pH of the mixture was adjusted at 8.7 to 8.9 using 0.5 N NaOH solutions. Appropriate reaction time was determined by gravimetric determination of unreacted residual formaldehyde. The basic recipe for the preparation of M-F pre-polymer and fragrant oil emulsion is given in Table 2.5.

Preparation of fragrant oil emulsion: Pre-determined amounts of Arabic gum, SLS, and Tween 20 were dissolved in DDI water, and fragrant oil was added. The emulsion of the fragrant oil was prepared using a homogenizer (Omni Macro Homogenizer, Omni Int., USA with 2000 to 5000 rpm at room temperature.

Microencapsulation: Encapsulation of the fragrant oil was carried out in a 1L-rounded flask via in- situ polymerization. The initial pH of the emulsion mixture was adjusted to around 7.5 using 0.5 N NaOH solution followed by addition M-F pre-polymer. For the poly-condensation of the separated M-F pre-polymer from aqeous phase, the pH of the emulsion was gradually decreased under different acid conditions (pH=5.0, 5.5 and 6.0) using 0.5 N citric acid solution for 2 h at 50°C.

After the completion of the encapsulation reaction, 5 to 6 drops of methanol was added as a quencher. A small amount of Arabic gum was added to prevent the destabilization of the microcapsules. The overall preparation scheme is illustrated in Fig. 2.25.

Characterization: The conversion or residual concentration of formaldehyde in the synthesis of M-F pre-polymer was determined by using gravimetry. The separation point of the M-F pre-polymer with varying pH of the continuous medium measured by a turbidity meter (TPS, WP89, Envioequip, Australia). Particle size and morphology of the microcapsules were measured using optical microscopy (SEM, JSM-5400, JEOL Co, Japan). Encapsulation efficiency was measured by thermo-gravimetric analysis (TGA-50, Shimadzu, Japan). H.Y. Lee evaporated fragrant oil from dried capsules above 120°C and this fragrant oil was defined as encapsulated oil.

The encapsulation efficiency was defined as follows;

Encapsulation efficiency (%) = Encapsulated oil (g) / Total oil used (g) X 100(%) (2.4)

The hardness of M-F poly-condensate was measured by the Vickers hardness method. Oil loss of dried microcapsules was characterized by gravimetry after drying at 150°C for 5 min. Thermo-stability of the capsules was characterized using differential scanning calorimeter (DSC) under nitrogen atmosphere. Weights were about 10mg, heating rate, 5°C/min, and the temperature range from 0-300°C.

Melamine formaldehyde pre-polymer: the representative overall reaction scheme of M-F pre-polymer is illustrated in Fig. 2.26. The M-F pre-polymer is well known as methylolmelamine. Two main steps are involved in the preparation of the M-F precursor (Jahromi 1999). First, nucleophilic addition reactions of melamine to formaldehyde under basic conditions result in random substitution of the amino groups and then to the synthesis of a mixture of methylolmelamine water-solubles. Next, two different types of linkage can result from the oligomerization by the formation of bridges between triazine rings: either between two methylol groups producing a methylene ether bridge or between a methylol group and an amino group producing a methylene bridges. Then, a large number of oligomeric derivatives and cross-linked network during poly-condensation reaction are formed (Kumar and Katiyar 1990, Coullerez et al. 2000).

Table 2.5: Basic Recipe for The Preparation of M-F Pre-polymer and Microcapsules.

Ingredients	**Amount (g)**
Melamine-formaldehyde pre-polymer	
DDI Water	41,6
Melamine	Variable[a]
Formalin (formaldehyde 37 % solution)	Variable[b]
NaOH (0,5 N aqueous solution)	Variable[c]
Emulsification	
DDI Water	100,0
Fragant oil	40,0
Arabic gum	2,0
SLS	1,0
Tween 20	1,0
Microencapsulation	
M-F pre-polymer	25
Emulsion	100
NaOH (0,5 N aqueous solution)	Variable[c]
Citric Acid (0,5 N aqueous solution)	Variable[c]

[a, b] Formaldehyde/ melamine (F/M) molar ratio was 2.3, 3.7, 5.5. Total weight of two ingredients was fixed at 100.0g.
[c] Appropriate amounts of these ingredients were used to adjust the pH of the reaction medium.

These bridge formations can be affected by many reaction parameters, such as pHs, F/M molar ratio, reaction temperature, and solid content. It is difficult to represent a M/F unit with a clear chemical structure and a well-defined repetition unit because of the wide variation in functionality, structure and reactivity of the intermediates involved in the reaction.

Fig. 2.27 shows the residual formaldehyde (wt% based on initial formaldehyde) against the reaction time. The F/M molar ratio was varied from 2.3 to 5.5. During the reaction, formaldehyde monomer was consumed almost linearly. As the F/M molar ratio increased content of the residual formaldehyde increased and the reaction reached an equilibrium state earlier. Arrows in Fig. 2.27 indicate the beginning of the reaction equilibrium state. Even at 1.1 F/M molar ratio, a small amount of formaldehyde monomer still remained without participating in the methylolmelamine

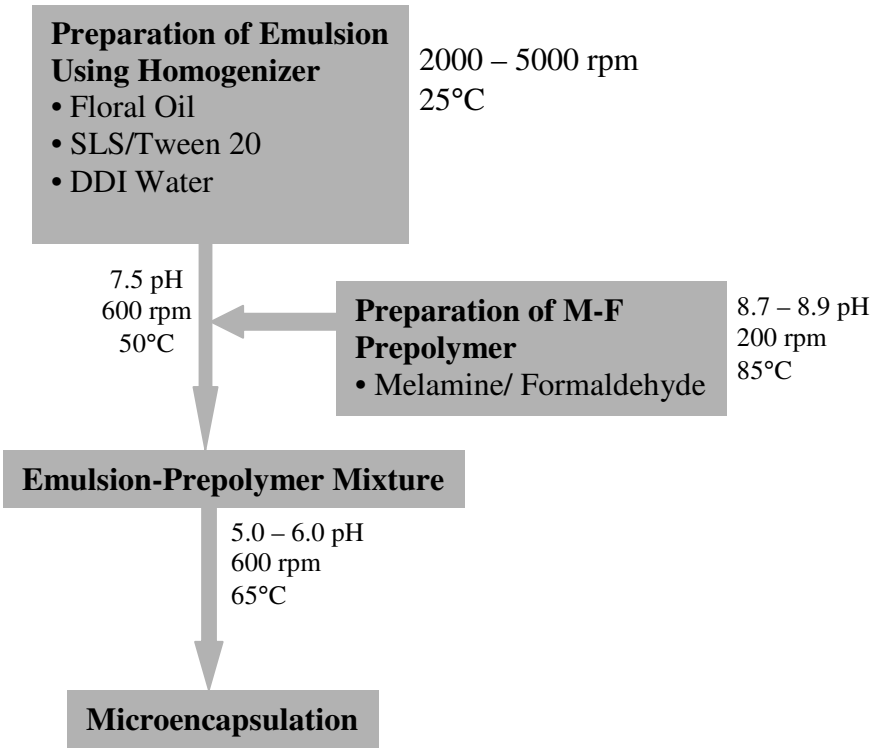


Figure 2.25: Schematic Representation of Microencapsulation Process [22]

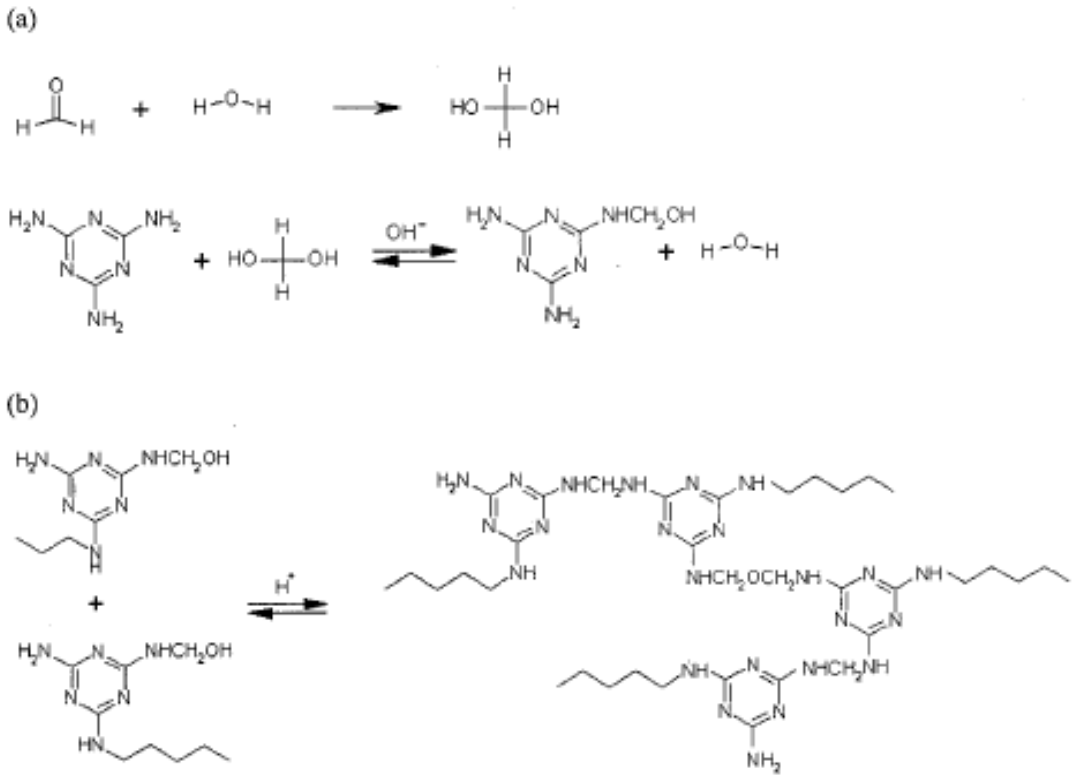


Fig. 2.26: Overall Reaction Scheme of Melamine-formaldehyde [22]

formation reaction. It was expected that this residual formaldehyde would react with water-soluble methylolmelamine to form water-insoluble precursor particles.

Separation of M-F pre-polymer: M-F pre-polymer in other words methylolmelamine mixture, is water-soluble initially the pH of the reaction mixture ws adjusted to 5.0 and 8.0 at the beginning of the reaction for the investigation of pH effect. Turbidity of the pre-polymer solution was monitored continuously without further pH adjustment with varying temperature. As the bridging reaction proceeds, solubility of the pre-polymer mixture decreased and eventually separated from its original continuous medium.

Fig. 2.28 shows the effects of F/M molar ratio and pH of the continuous medium on the separation condition. Solubility of the pre-polymer mixture increased as the reaction temperature increased. As can be seen in Fig. 2.28, at high F/M molar ratio, the separation time was shortened at a constant reaction (for separation) temperature. In principle, two different types of bridges may be formed leading to methylene or ether bridges according to the pH and F/M molar ratio, which affects the solubility of the pre-polymer mixture (Kumar and Katiyar 1990).

Ether bridges can be formed easily in a high F/M mole ratio, as illustrated in Fig 2.26, and it was expected that methylolmelamine derivatives with high functionalities would be obtained easily at a high F/M molar ratio.

It can be seen that F/M molar ratio depends on the separation temperature at the same reaction time, whereas the pH effect is not so significant. At low pH, the pre-polymer mixture became turbid rapidly. However, it was observed that neither separation temperature nor time depends on pH of reaction medium. As mentioned above, pH was not adjusted but it decreased continuously during the reaction. The pH decreased during the reaction, which was attributed to the formation of formic acid according to the so-called Canizarro reaction (Jahromi 1999). Eventually, this reaction reduced the pH to accelerate the poly-condensation of M-F pre-polymer. Characteristic of microcapsules; Fig 2.29 shows floral oil emulsion (a) and microcapsules (b), (c) and (d) with varying pH at a 5.5 F/M molar ratio. The droplet size of the floral emulsion ranged from 3-8 μm. The average particle size depends on surfactant (or stabilizer) level/ type, homogenizer speed/ time, and type of oil. After the preparation of the stable emulsion, M-F pre-polymer was injected at 50˚C.

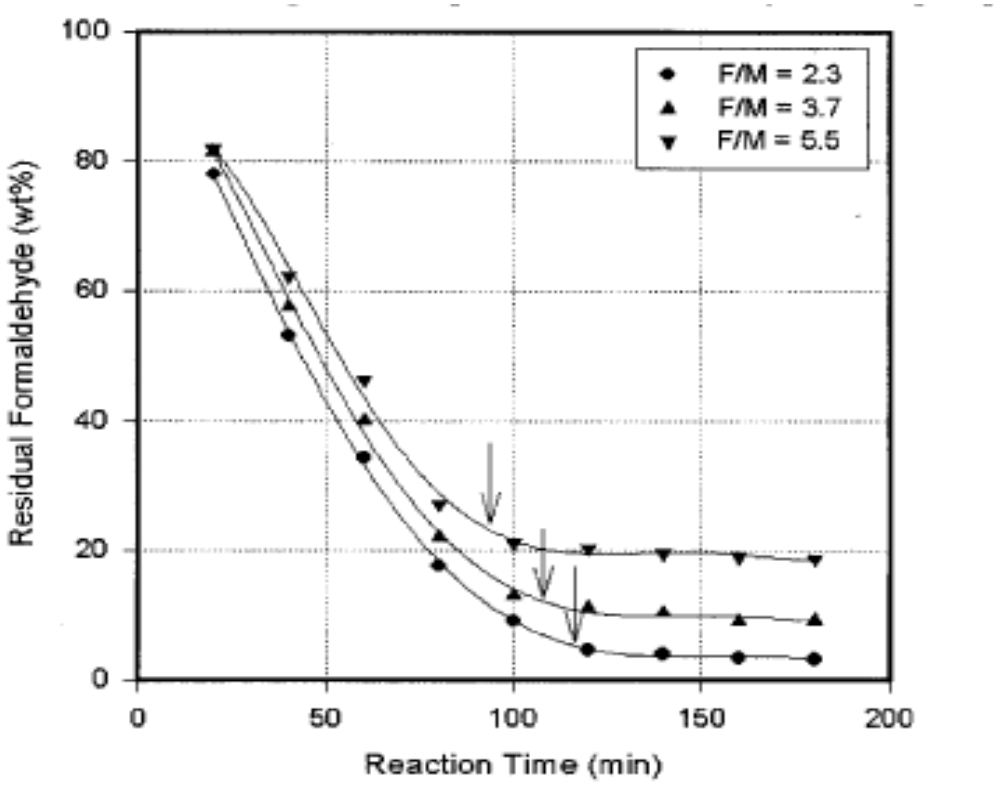


Figure 2.27: Residual Formaldehyde Against Different F/M Molar Ratio in the Preparation of M-F Pre-polymer [22]

The pH in the encapsulation process varied from 7.5 to 5.0 (b), 5.5 (c), 6.0 (d), respectively, in Fig. 2.29 using 0.5 N citric acid solution. The average size of the microcapsules was 15 (b), 13 (c) and 12 μm (d), respectively. As pH increased, the average particle size of the microcapsule decreased and its surface became smooth.

At low pH, the surface morphology of the microcapsule decreased was similar to that of a raspberry. This suggested that aggregates or premature particles, which were formed from condensation reaction among methylolmelamine oligomers, adsorbed onto oil droplets. Further condensation reactions between the premature particles on the droplet surface consolidate the wall of the capsules. As mentioned earlier, the formation of methylene bridge is favorable at low pH, whose water-solubility would be lower than that of ether bridges. Therefore, individual particle consist of network M-F precursors that can be formed immediately without liquid-liquid separation from the aqueous phase onto the oil droplet interface.

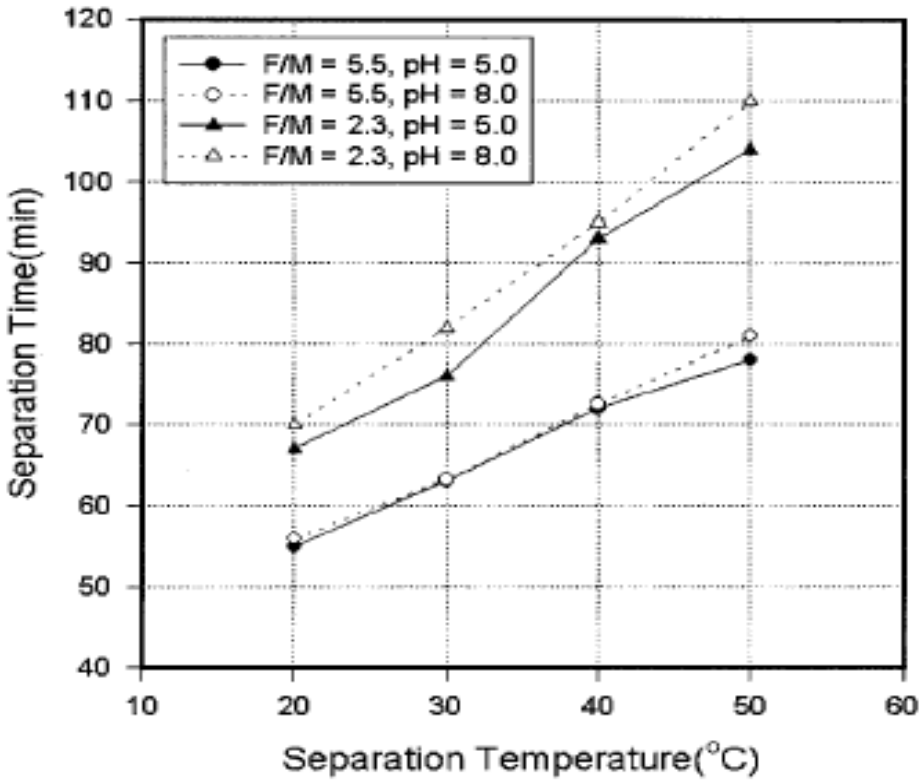


Fig. 2.28: Separation Temperature and Time for M-F Precursor with Varying F/M Molar Ratio and pH [22]

Capsulation efficiency: the existence of floral oil in the microcapsule was easily verified by optical microscopy. Fig. 2.30 shows microcapsules containing floral oil (a) and released oil and cracked microcapsules (b) under pressure. Table 2.6 shows the capsulation efficiencies of the floral oil with varying pH and F/M molar ratio. It was found that the pH did not significantly affect the efficiency. However, as the F/M ratio increased from 2.3 to 5.5, the efficiency increased. The efficiency was not determined solely by the separation condition of methylomelamine but by both F/M molar ratio and pH. High encapsulation efficiency can be obtained when the wall material shows a good thermo-mechanical resistance. In fact, microcapsules prepared under low F/M molar ratio and low pH was crushed easily during drying process by gravity. It was found that the low value of the efficiency was mainly attributed to deformation of the shell during the heating and drying process. Oil loss was measured by gravimetry under the conditions of 5 min and 150˚C. The oil loss increased from 6-25 wt % when the F/M molar ratio decreased from 5.5 to 2.3. As can be seen in Table 2.7, it can be expected that high F/M molar ratio gives low hardness but high flexibility. As the F/M molar ratio decreased, however, the M-F poly-condensate became more brittle.

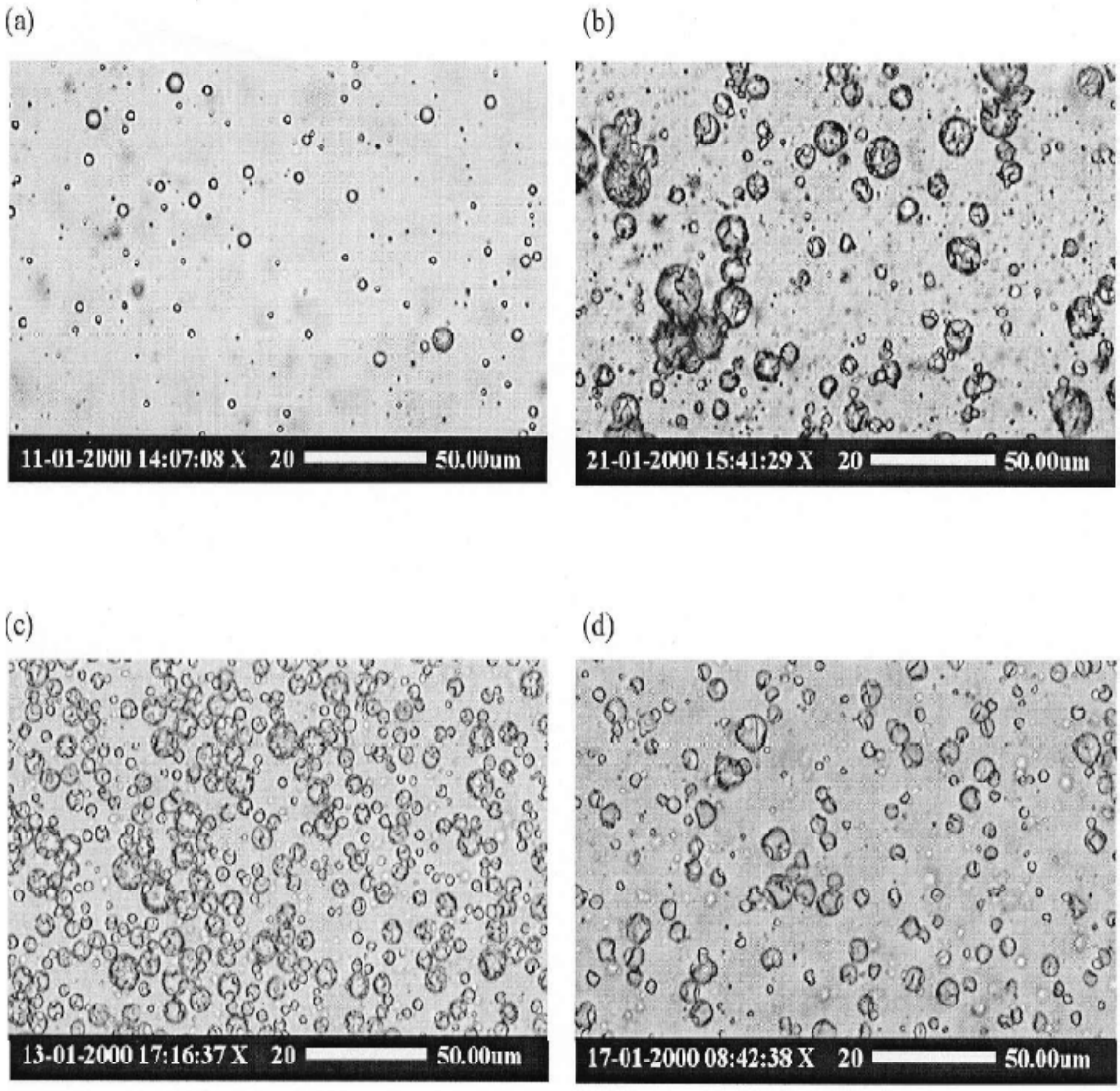


Fig. 2.29: Optical Microscopy Photographs of Fragrant Oil Droplet (a) and Microcapsules Prepared with Different pH; (b) 5.0, (c) 5.5, (d) 6.0 [22].

Fig. 2.31 shows the DSC curves for the microcapsules prepared with varying F/M molar ratio. As can be seen in Fig.2.31, the main relaxation peaks were shifted to a higher temperature region as the F/M molar ratio decreased. All these transition temperatures were higher than 150˚C.

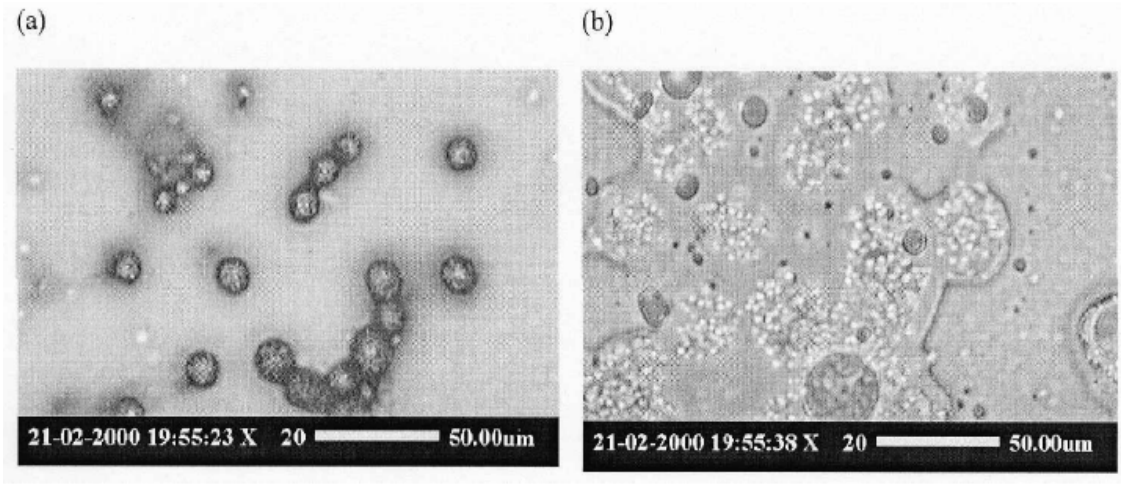


Fig. 2.30: Optical Microscopy Photographs of Dried Microcapsules (a) and Released Fragrant Oil and Crushed Capsules Under Pressure (b) [22].

Table 2.6: Encapsulation Efficiency with Varying F/M Molar Ratio and pH [22].

Process Variables	**Encapsulation efficiency (%)**
At 6.0 Ph	
F/M= 2,3	67,2
F/M= 3,7	72,1
F/M= 5,5	81,4
At F/M=5,5	
pH= 5.0	73,8
pH= 5.5	76,0
pH= 6.0	81,4

Fig. 2.29 shows the microcapsules containing floral oil that were prepared under different pH and F/M molar ratios. The pH values in Fig. 2.29(a) and (b) are 6.0 and 5.0, F/M molar ratio 5.5 and 2.3, respectively. It was observed that surface morphology of the microcapsules was different with varying F/M molar ratio and pH of the reaction medium. As the pH decreases, formation rate of M-F precursor increases consequently to accelerate the formation of individual M-F particles during the phase separation (Samejima et al. 1982). A number of small M-F particles were observed in the case of low pH and F/M molar ratio. The surface of microcapsules in Fig. 2.29 (b) was raspberry-like and seemed to be composed of aggregates of the M-F particles. This polynuclear morphology has been reported by Sheiham and Templey (1992) in the preparation of microcapsules for carbonless paper. From this result, it was expected that a competitive reaction occured between the separation/ solidification of M-F precursor and the formation of individual M-F particles in the aqueous phase.

Table 2.7: Hardness with Varying F/M Molar Ratio [22]

F/M Molar Ratio	Hardness[a]
2.3	23
3.7	14
5.5	10
[a]Hardness of copper: 30 – 40; steel: 100	

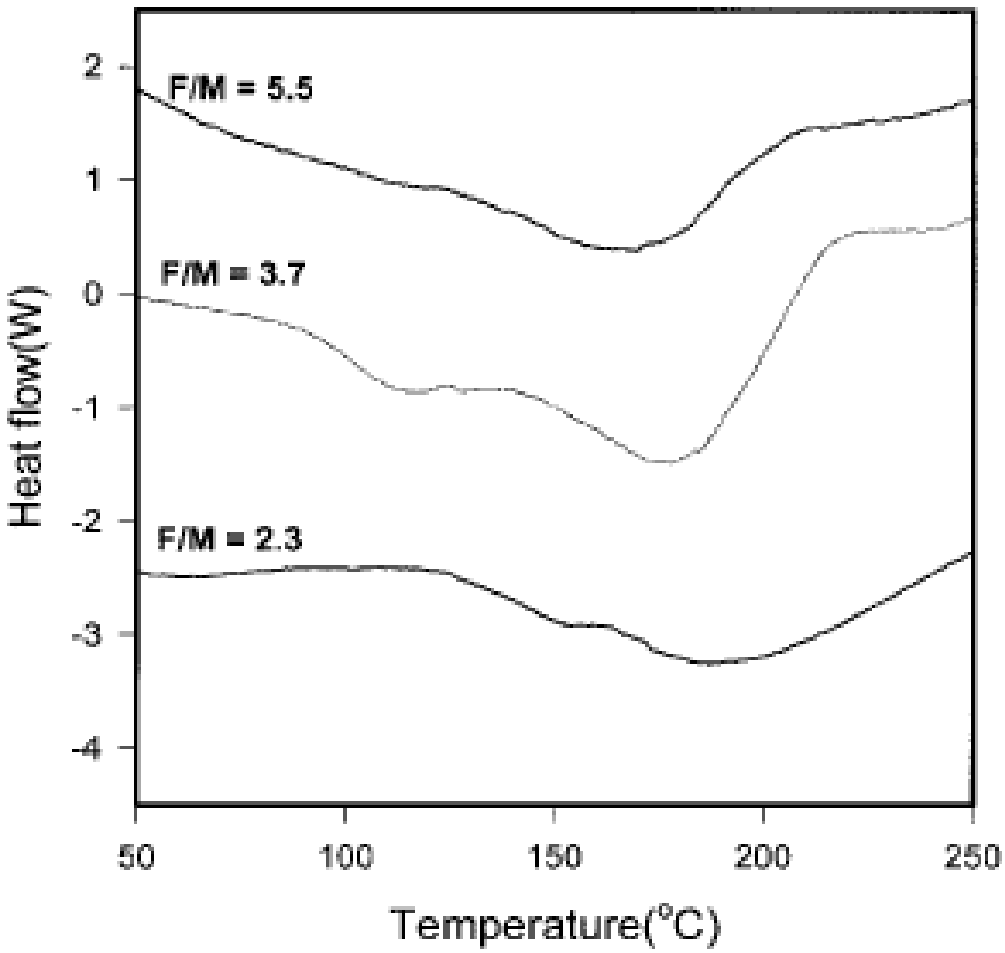


Fig. 2.31: DSC Curves of Microcapsules Containing Floral Oil with Varying F/M Molar Ratio [22]

It was concluded that the separation condition of M-F pre-polymer significantly determined the surface morphology and encapsulation efficiency.

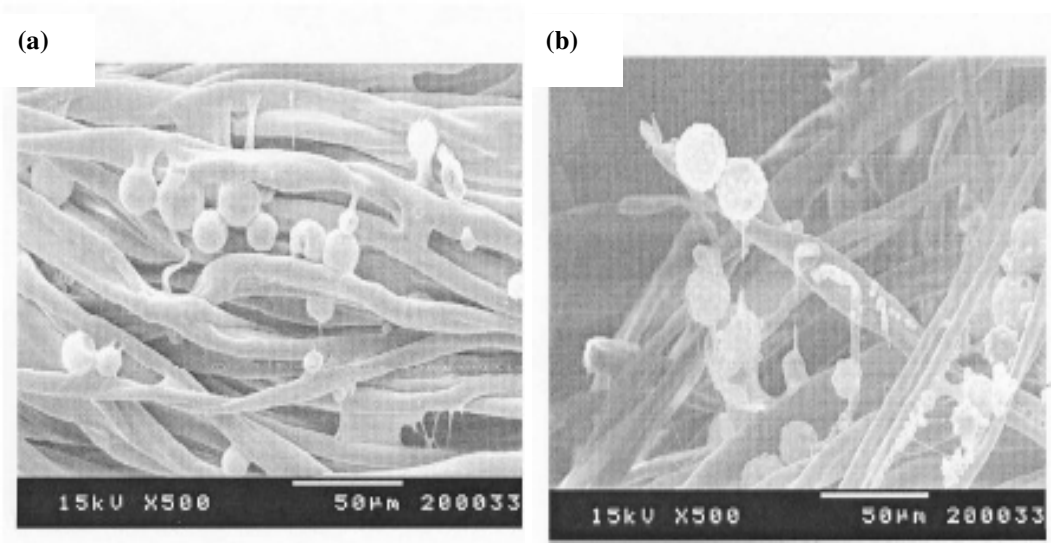


Fig. 2.32: SEM Image of Microcapsules Containing Floral Oil Attached onto The Cotton Fiber; (a) pH=6.0, F/M =5.5; and (b) pH=5.0, F/M =2.3 [22].

2.4.3. Shell Structure of Melamine/Formaldehyde (MF) and The Effect of Shell Material Dropping Rate (Immersion Rate)

Similar to the study of H.Y.Lee, S.J.Lee, I.W. Cheong and J.H.Kim [22]; Junfeng Su, Lixing Wang and Li Ren [23] also made some researches on MF microcapsules, however, they analyzed MF microcapsules from different perspective and in their study, they used phase change material (PCM) as active ingredient in the core of the microcapsule. An in-situ polymerization process prepared a series of melamine formaldehyde (MF) microcapsules containing phase change material (PCM) as core material. The phase change temperature of this PCM was 24°C and its phase transition heat was 225.5 J/g. The microencapsulated phase change materials (MicroPCMs) were bedded in in-door wall materials to store and release heat energy, which would economize heat energy and make the in-door condition comfortable. Junfeng Su, Lixing Wang, Li Ren in 2005 investigated the structural formation mechanism by microscope and scanning electron microscopy (SEM). The superficial morphology measurements indicated the optimal shell material dropping rate 0.5 ml/min, double shell, and temperature elevating speed 2°C/10 min. The results obtained in the present investigation were reasonably understood on the basis of getting determinate rigidity and compacted shell. Also, the observed results were used to control the mass of shell material to get desired thickness of shell.

In recent years, much attention is focused on energy problems and many researchers have done the research and development. Phase change material (PCM) has been widely studied and applied for thermal energy storage. As PCM can absorb, store, and release large amounts of latent heat over a defined temperature range while itself changes phase, it can be used in may fields. Microencapsulated phase change materials (MicroPCMs) have attracted more and more attention since the 1990s. MicroPCMs offer a measure to solve the super-cool problem and inter-facially combine with circumstance materials. MicroPCMs have been synthesized with urea-formaldehyde, cross-linked nylon, melamine-formaldehyde (MF), gelatin-formaldehyde, and polyurethane as shell materials, which are usually used at a temperature lower than 150 °C. These microPCMs were used in functional fiber, solar energy utilize, heat energy transfers, agriculture, and building materials.

MicroPCMs should have appropriate properties, such as superficial morphology, diameter distribution, thermal prosperities, shell mechanical strength, shell thickness, penetration property, etc. Especially, for the microPCMs, the shell properties, including mechanical strength, shell thickness, and shell penetration, which affect stability of microcapsules, are the main characteristics needed in application.

However, the structural formation process of microPCMs has rarely been studied as a key problem. It is the basic of to getting determinate rigidity and compacted shell, by depositing shell on core particulates. Also, relationship of the process details of emulsification and core-shell structures is of great value, but few were reported.

The microPCMs were prepared by using in situ polymerization with prepolymer of MF. It was investigated that structural formation process of microPCMs by microscope and scanning electron microscopy (SEM) analysis for the cross sections of microcapsules, which revealed the systematic formations of deposit structures followed by the formation of core-shell structures. Moreover, the superficial morphology measurements indicated the optimal shell material dropping rate. Also different shell material dropping rate affected the thermal properties of microPCMs. The microPCMs preparation was interpreted in terms of structural formation of the microcapsules.

In their study, the pre-polymer of melamine-formaldehyde (MF) was obtained from Shangai JQ chemistry Ltd. Co of China, whose solid content was 50±2 wt %. The

composite PCMs that were prepared by Energy sources and Low emission Research Institute of Hebel University of Technology was applied as core material. The temperature of solid-liquid phase change was 24°C and phase change quantity of heat was 225.5J/g. Stryene maleic anhyride random copolymer solid (Scripte-520) was used as a dispersant. Nonionic surfactant, NP-10 ((poly(ethylene glycol) nonylphenyl) obtained from Sigma Chemical was used as an emulsifier. The encapsulation was carried out in a 500 ml three-neck round-bottomed flask equipped with a condensator and tetrafluoroethylene mechanical stirrer. First, 10 g styrene-maleic anyhdride, 0.2 g nonionic surfactant NP-10, as emulsifying agents, and 0.8 g NaOH were dissolved in 100 mL, 50 °C water, whose pH value was 4-5 after 2 h. Thirty two grams core was added to aqueous surfactant solution, and the mixture was emulsified mechanically under a vigorous stirring rate of 3000 r/min for 10 min using QSL high-speed disperse-machine (Shangai Hongtai Ltd., China). Then dropped the emulsion in the bottle dipped in steady temperature flume and stirred at a speed of 1500 r/min, and dropped 16 g pre-polymer at a rate of 0.5 ml/min. The shell formed after 1.5 h by heating slowly to temperature of 60 °C. Then another 16 g pre-polymer was dropped in bottle at the same dropping rate. Then the temperature elevated to 75 °C. After polymerization for 1 h, temperature was dropped slowly at 2 °C/min to room temperature. The resultant microcapsules were filtered and washed with water and dried in a vacuum oven.

Testing; the method of studying the structural formation process of microPCMs is to observe the photos of emulsion, which batch extraction during the microcapsules formation process. One ml of the microcapsules in emulsion was paved on a stainless glass slice and air-dried; photos of the morphology of the microcapsules were taken by optical microscope. After microcapsules were dried in a vacuum oven at 40 °C for 24 h, the surface morphological structure was examined by means of an XL30 PHILIPS scanning electron microscopy (SEM). The thermal properties of the dry microcapsules were observed by using a differential scanning calorimeter (DSC, Perkin-Elmer, DSC7) at a rate of 10 °C/min in a nitrogen atmosphere. FTIR transmittance of pure PCM, microcapsules, and the shell material were obtained by using a Perkin-Elmer 2000 spectrophotometer (wave-numbers 400-4000 /cm.)

Effect of emulsification: based on the studies conducted, it is figured out that mass ratio of core and shell of MicroPCMs was 3:1 to ensure the microcapsules had good

heat storage function. With the increase of ratio of core material, the compatibility decreased, whereas shell thickness decreased.

Analysis of structure formation: optical microphotographs of microcapsules containing PCM emulsified 3000 r/min were taken on the study of structural formation process during polymerization in water. It was studied that the facts of shell material dropping rate, different dropping times, and different temperature elevating speed.

First, to get details of the process, it is extracted one drop of the microcapsule dispersion 4 times each at the end of encapsulation after temperature elevating speed of 10 °C/10 min, which were placed on a glass plate and air-dried, photos of the shape of the microcapsules were taken by optical microscope. It was easy to obtain the diameter of the microcapsules and shell material deposit morphologies from the photographs. Fig. 2.33 (a-d) shows the photographs of different shell material dropping rates of dropping all directly, 5 ml/min, 1 ml/min, and 0.5 ml/min, respectively. Dropping rate of shell material could control the morphology of microcapsules.

With the increase of dropping rate of shell material, the surface was rougher. Moreover, when the shell material dropped all once as Fig. 2.33 (a) shows, the shell thickness was not regular and not accordant. The reason is that the pre-polymer of MF will not capsulate on core slowly and tightly at rapid dropping rate. So at same core emulsify stirring speed and same mass ratio of core and shell material, different thickness of shell also gets different penetration property. Dropping rate of 0.5 ml/min is the perfect result. As the core material could not be encapsulated completely and the shell material also could not absolutely cover the core, in Fig. 2.33 (b) there were little polymers pilling between microcapsules.

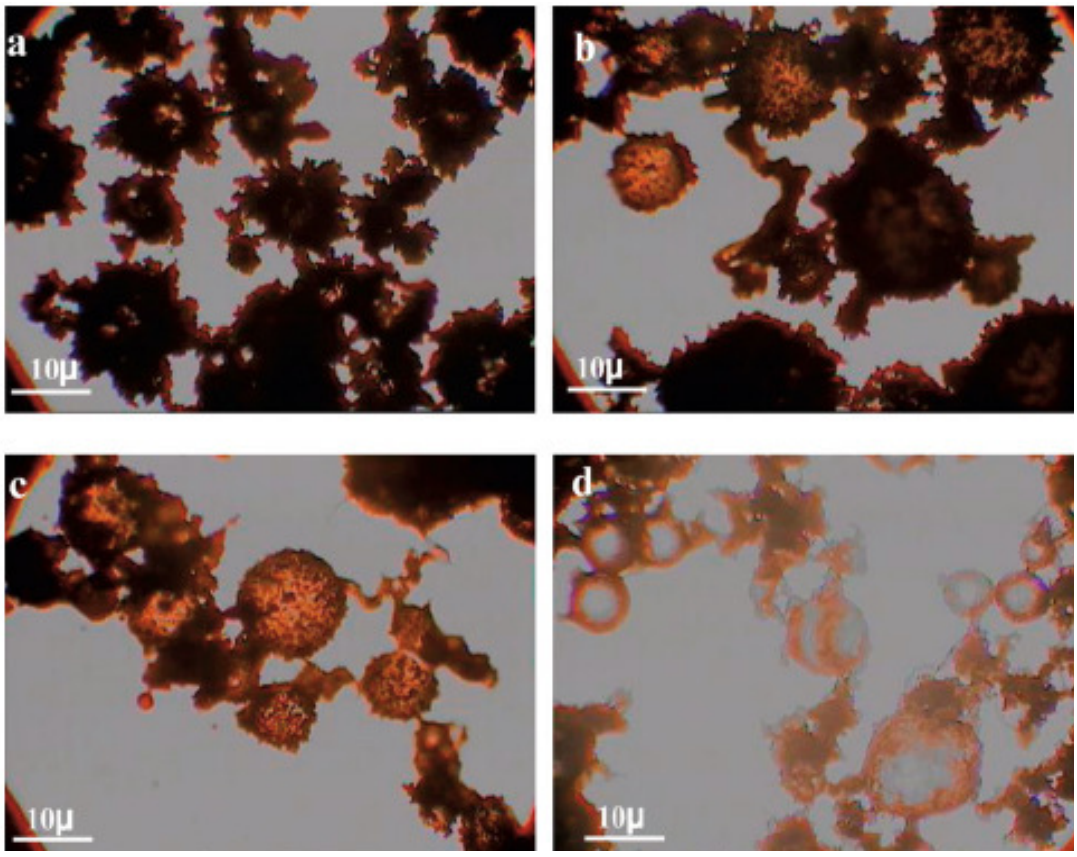


Fig. 2.33: Optical Microphotographs of MicroPCM, Made of Different Shell Material Dropping Rate of Dropping All Once (a) 5 ml/min, (b) 1 ml/min, (c) 0.5 ml/min. [23]

At the same liquid shell material dropping rate of 0.5 ml/min, Figure 2.34 shows different temperature elevating speed of 2 °C/10 min, Figure 2.33 (a) and 5 °C/10min, Figure 2.34 (b). The temperature elevated to 75 °C from the shell material dropping over. After 1 h, the temperature dropped to room temperature and microcapsules solution is diluted. 2.34 (b) shows there were some polymers, which was not deposited covering microcapsules. Above all, the shell material was dropped continuously and formed single-shell. The double-shell microPCMs were prepared by dropping shell material twice. First, dropped the emulsion in the bottle dipped in steady temperature flume and stirred at a speed of 1500 r/min while 16 g pre-polymer was added at a speed of 0.5 ml/min. The shell formed after 1.5 h by elevating the temperature to 60 °C slowly. Then another 16 g pre-polymer was dropped in bottle at the same dropping rate. Then the temperature elevated to 75 °C. As Figure 2.35 shows, the double-shell microcapsules surface is smooth and compact.

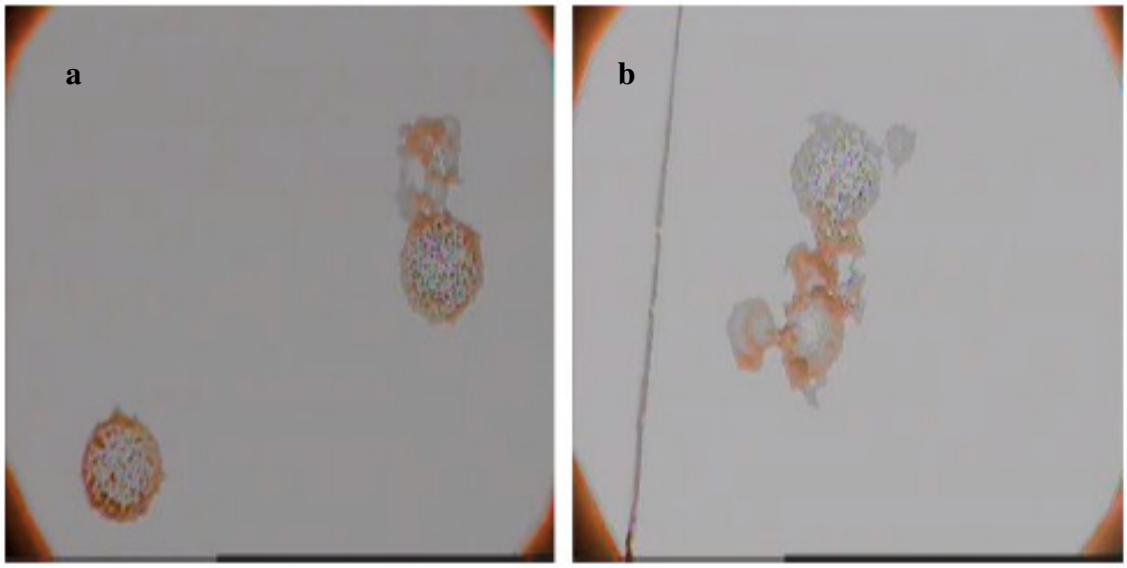


Figure 2.34: Optical Microphotographs of MicroPCM, Made by Different Temperature Elevating Speed of 2 °C /10 min (a) and 5 °C /10 min (b), At The Same Liquid Shell Material Dropping Rate of 0.5 ml/ min. [23]

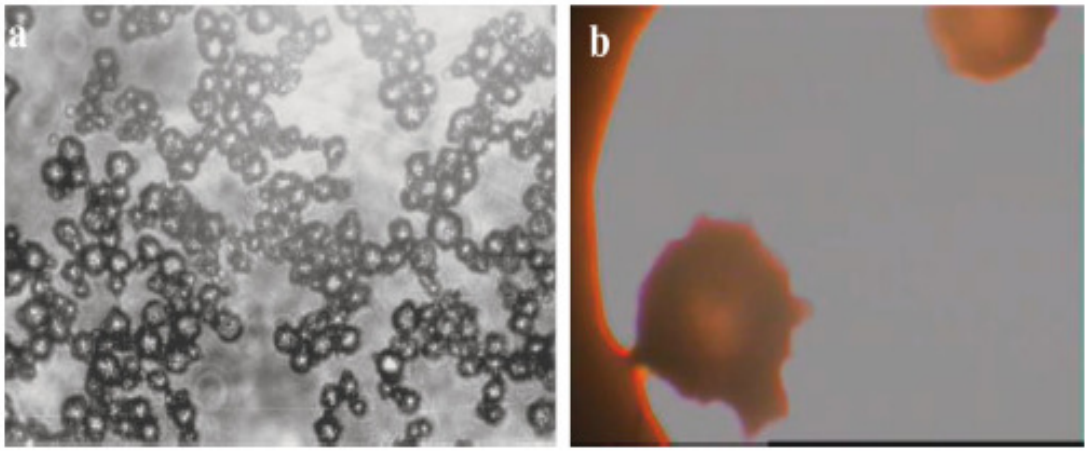


Figure 2.35: Optical Microphotographs of Double-shell MicroPCM, Showing The Microcapsules Surface are Smooth and Compact [23]

Surface morphology: after double-shell microcapsules were dried in a vacuum oven at 40 °C for 24 h, SEM photographs reflected the surface morphologies. As Fig. 2.36 (a) (1000X) shows, the surface of most of the microcapsules was smooth and the shape was very regularly global, with average diameter of about 5 μm. The core material could not been encapsulated completely and the shell material also could not absolutely cover on the core, in Fig. 2.36. (b) (5000X), there was little polymer pilling between microcapsules. With the increase of dropping rate of shell material, Fig. 2.36 (c) (10.000X), the surface was rougher. This is probably because the pre-polymer of MF will not capsulate on core slowly and tightly at rapid dropping rate.

The surface is smooth and shell protects the PCM not affected by the outer materials and environment.

Thermal properties: the thermal characteristics of the microcapsules containing PCM are shown in Fig. 2.37 and Fig. 2.39**,** using of TG and DSC. According to TG analysis presenting residual weight (%) of material by temperature change, the microcapsules weight was decreased with increasing temperature. In Fig. 2.37 pure PCM lost weight at the temperature of 137 °C and lost completely at 207 °C. The loss of weight was rapid. Contrastively, microcapsules containing PCM lost weight at the temperature of nearly 100 °C. The lost weight was some water and other little molecule ingredients. From 271 °C, because of the cracking of shell of microcapsules, the weight loss was more rapid and was lost completely at 440 °C. Microcapsules weight loss ratio was lower than that of pure PCM obviously. Thus, it proved that double polymer shell protected the PCM.

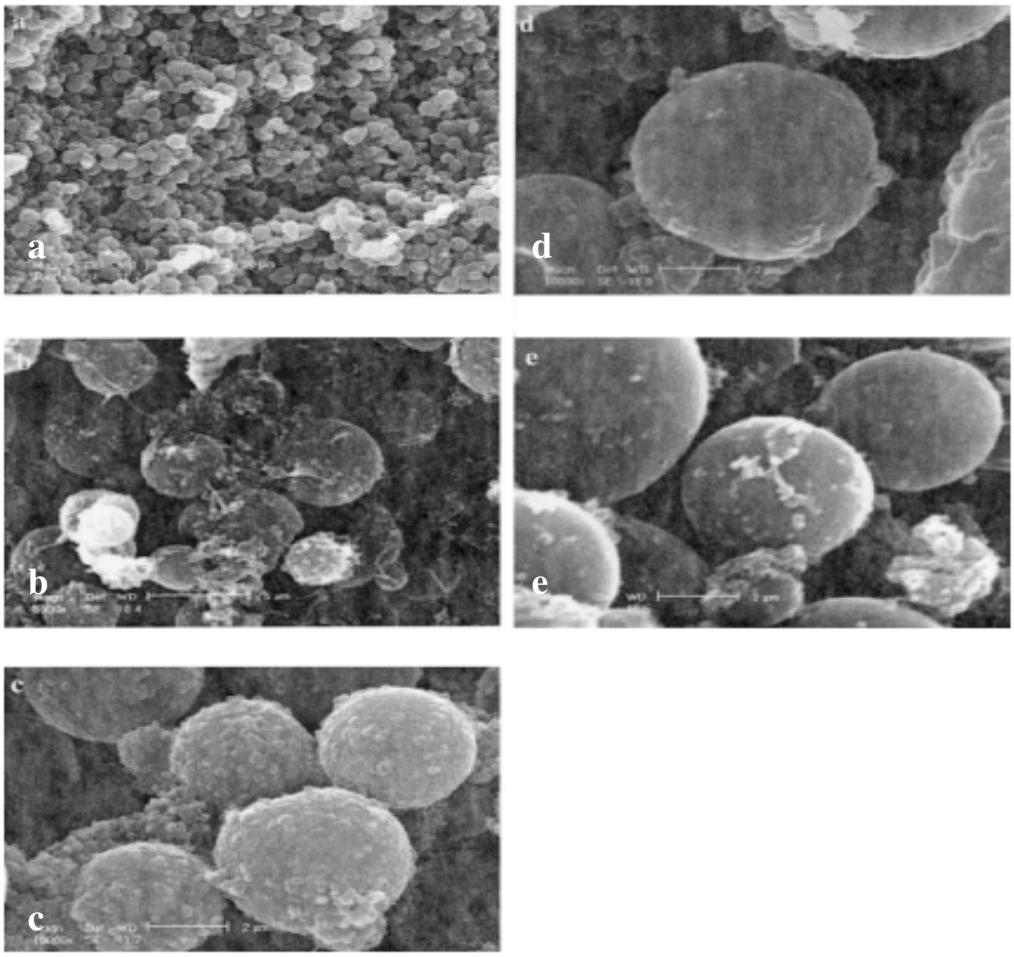


Figure 2.36: The SEM Photographs of Double-shell Microcapsules Morphologies, Dried in a Vacuum Oven at 40 °C for 24 h. (a) x 1.000, (b) x 5.000, (c)-(e) x 10.000 [23]

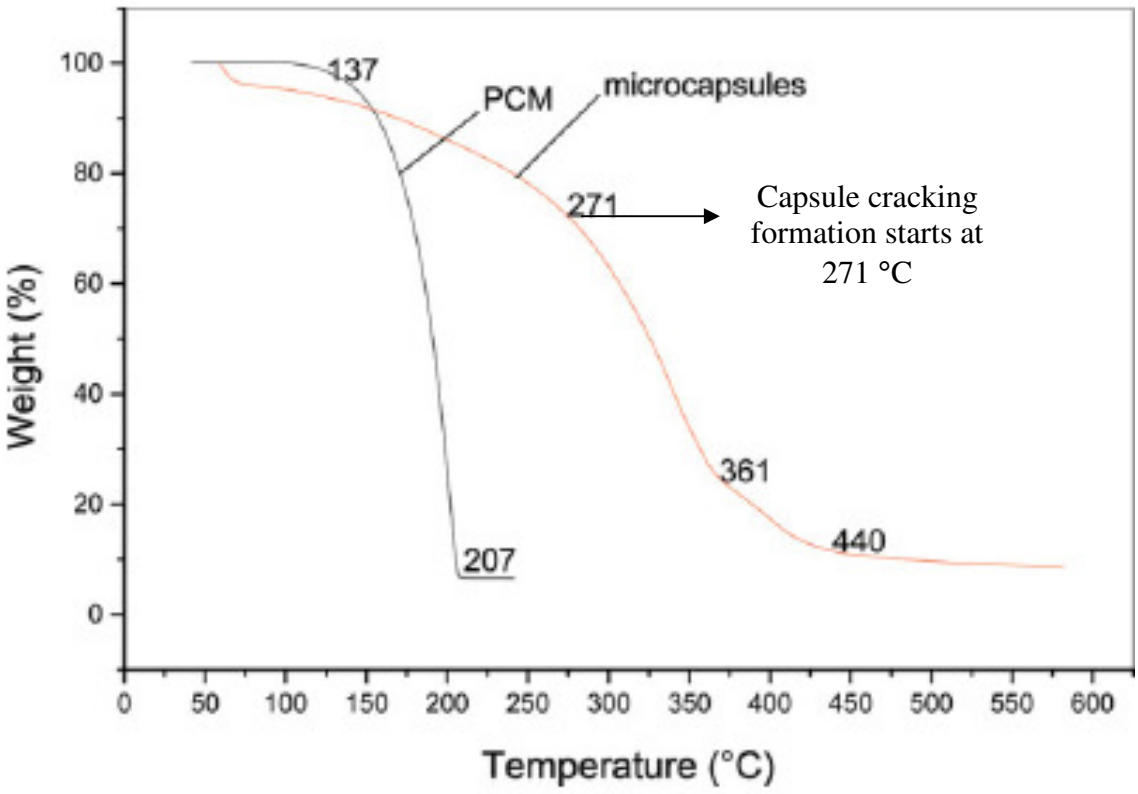


Fig. 2.37: TG Curves of Pure PCM and Double-Layer MicroPCMs [23]

To know the compactness of different encapsulation effect, it was compared TG curves of the following microPCMs made by different layers, shell prepolymer dropping rate, and temperature elevating speed, such as that shown in Fig. 2.38. Obviously, the best is the microcapsules of two layers, 0.5ml/min dropping rate, 2 °C/10 min temperature elevating speed. It also can be found that the lost weight temperature of two layers microPCMs is higher than that of one layer. Thus, it proved that double-layer polymer shell protected the PCM compacter.

Fig. 2.39 shows DSC curves of same weight of pure PCM and microPCMs. As microcapsules were composed of PCM and shell material, phase change heat of microPCMs was less than that of pure PCM. Also, onset temperature of melting peak is 1 degree higher than that of pure PCM. The reason is that the shell polymer has a resistance thermal transition. But it will not affect storage and release heat energy, which will economize heat energy and make the in-door condition comfortable.

In conclusion, the factors influencing thermal stability were investigated in relationship with the shell structures of microPCMs. Thus, this study has demonstrated that the shell structures of microPCMs can be controlled by structural formation process, including shell material speed of 0.5 ml/min, temperature elevating speed of 2 °C/ 10min and shell material dropping twice.

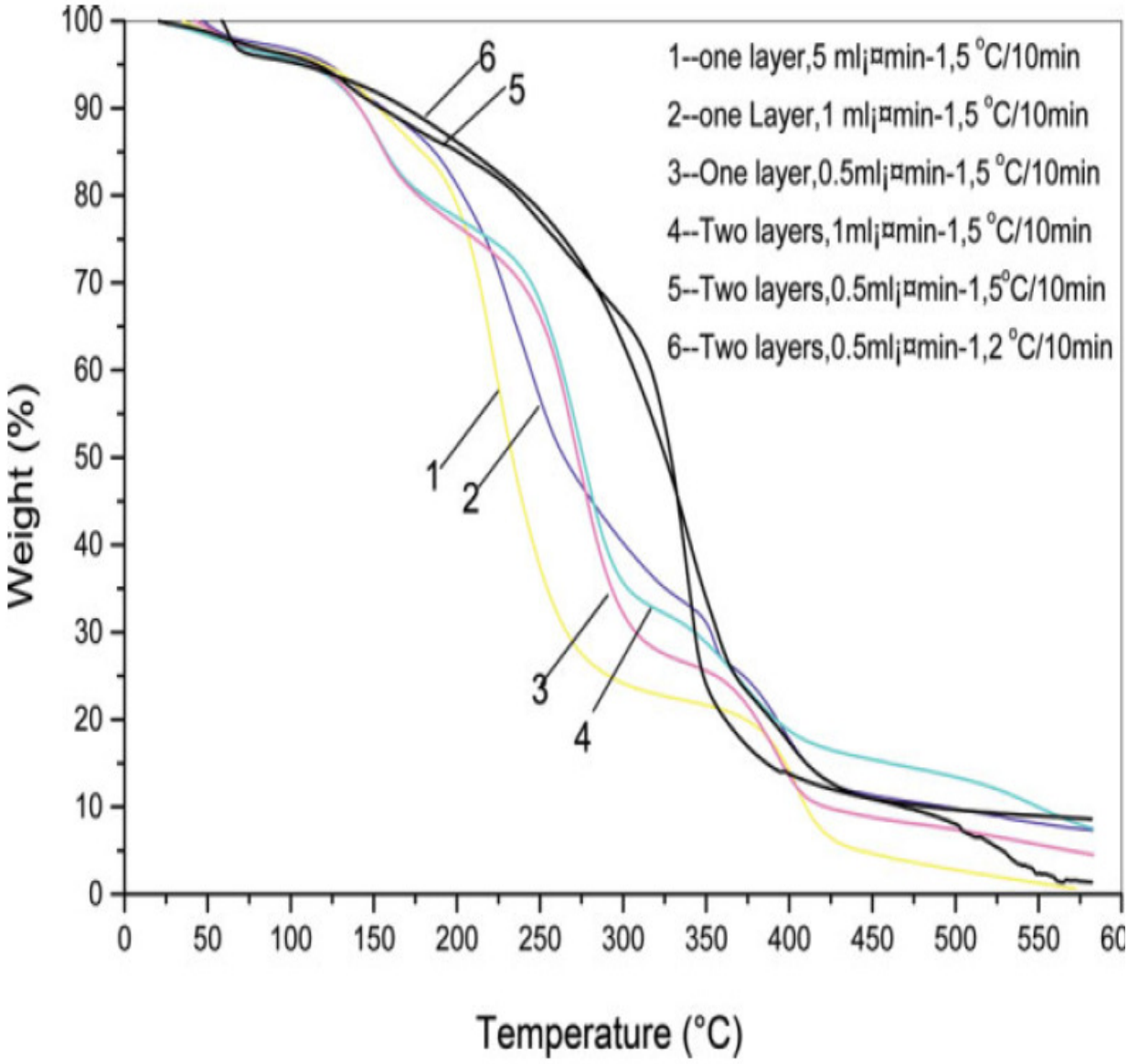


Figure 2.38: TG Curves of MicroPCMs Made by Different Layers, Shell Pre-polymer Dropping Rate, and Temperature Elevating Speed [23]

To get perfect thermal properties, surface morphologies and shell structure of microcapsules are crucial. The investigation by DSC shows the melt point of PCM in shell does not change and the heat transmit is obvious.

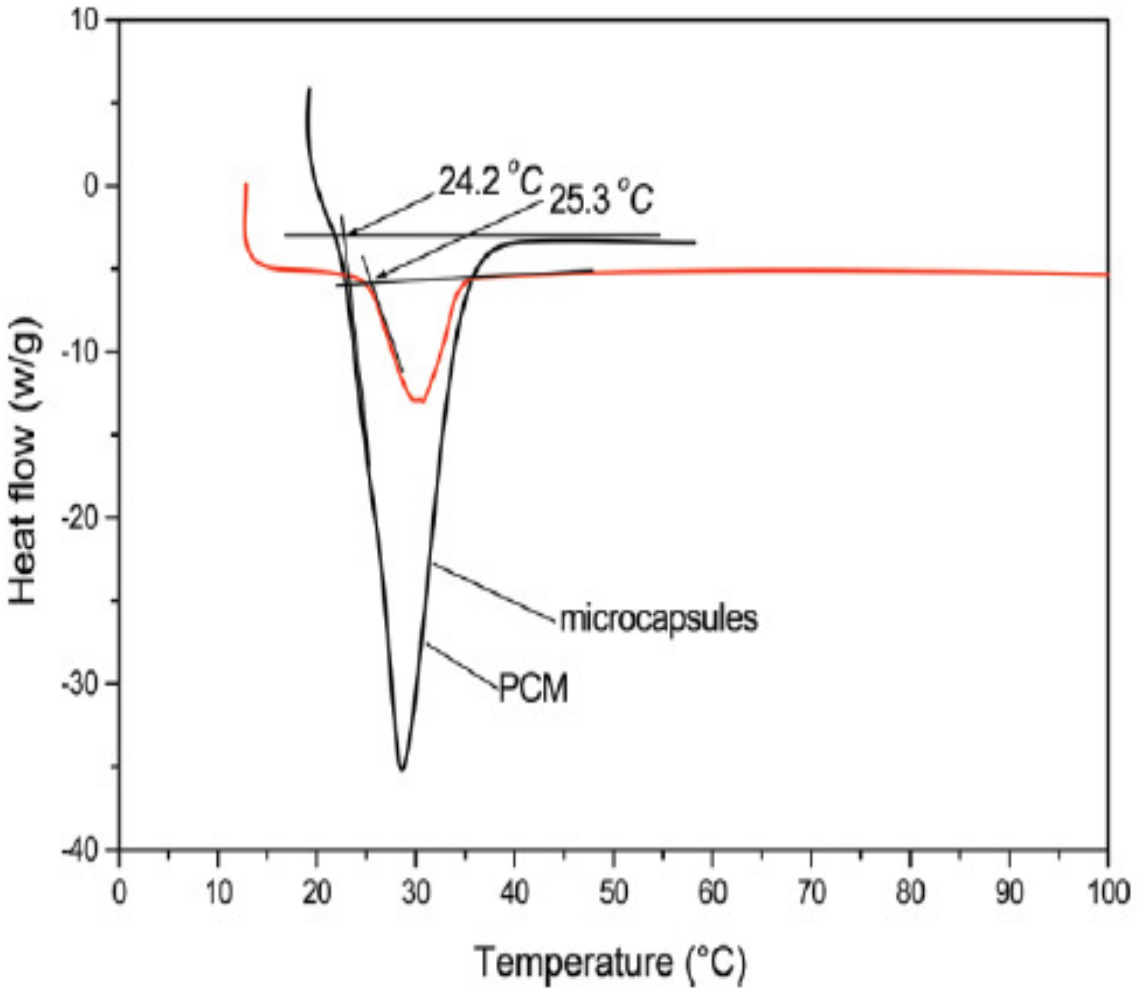


Fig. 2.39: DSC Curves of Same Weight of Pure PCM and MicroPCMs [23]

The results of this study are summarized in Table 2.8 below.

Table 2.8: Summary of The Study of Junfeng Su, Lixing Wang and Liren

Condition	Result	Reason
Increase of dropping rate	Surface of the microcapsules will be rougher.	Because, the pre-polymer of MF will not capsulate on core slowly and tightly at rapid dropping rates. Dropping rate of 0.5 ml/min. is the perfect result to obtain smoother surfaced of microcapsules.
Mass ratio of core and shell of MicroPCMs should be 3:1	Having a good heat storage function.	Because, any increase of ratio of core material, the compatibility decreased, whereas shell thickness decreased.
Double shell instead of single shell	Double shell microcapsule surface is smooth and compact	Therefore, double shell microcapsules protect the PCMs inside of it and they have much resistance to outer conditions such as temperature increase etc.

2.5. Mechanical Properties of Microcapsules

To be able to analyze and to be able to have a better understanding of the mechanical properties of microcapsules, different capsule membranes were investigated and the strength of the capsule walls was examined in detail by many researchers. Capsule deformation and capsule bursting are the two major parameters that were concentrated in those previous studies.

2.5.1 Mechanical properties of melamine-formaldehyde microcapsules

In the study of G.Sun, Z.Zhang [24], melamine-formaldehyde microcapsules prepared by in-situ polymerization have impermeable walls. They have been widely used in carbonless copy paper, by far the largest commercial application for the microcapsules [25], and other pressure-sensitive products such as carriers for fragrant oils (Hong and Park 1999), pest repellents [26], and adhesives [27]. For all these applications, understanding of the mechanical properties of the microcapsules is essential for improving the quality of the products. However, little such information is available, mainly because of their small sizes, typically 1-10 μm in diameter when used for carbonless copy paper.

Recently a micromanipulation technique has been developed to measure the bursting force, diameter of single melamine-formaldehyde microcapsules, and the relationship between the forces imposed on the single microcapsules and their deformation [28]. The microcapsules investigated were as small as 1 μm in diameter. This technique has been further used to measure the mechanical properties of single melamine-formaldehyde microcapsules, which include elastic, visco-elastic or plastic behaviors, and the results are presented.

In this study, melamine-formaldehyde microcapsules were prepared based on the formulation procedure recorded in a UK patent [29]. However, certain modifications on this procedure were made.

The core material encapsulated was a 10:1 (w/w) mixture of HB40 and kerosene; the former being a mixture of technical grade partially hydrogenated terphenyls (Monsanto Limited, Brussels, Belgium). The microcapsule wall was formed by R1144 copolymer, a technical grade acryl amide/acrylic acid copolymer (Allied Colloids Ltd., Bradford, UK), and technical grade BC336 melamine-formaldehyde

pre-condensate (British Industrial Plastic Ltd., Birmingham, UK). Microcapsules were prepared according to the following procedures:

a) 23 g of R1144 copolymer was mixed with 20 g of BC336 pre-condensate and 280 g of deionized water,

b) The pH of the solution was lowered to 4.3 by adding acetic acid then stirred for 105min,

c) At 15˚C, 90 g of the core material was added into the solution, and the mixture was emulsified at 2500 rpm for 30 min,

d) Stirred the dispersion for 30 min at 15˚C,

e) The temperature was increased to 55˚C. At this temperature, the dispersion was continually stirred for 3 h. The microcapsules were then found to have formed, and

f) Raised the pH of the dispersion to 10 by adding 20% NaOH solution.

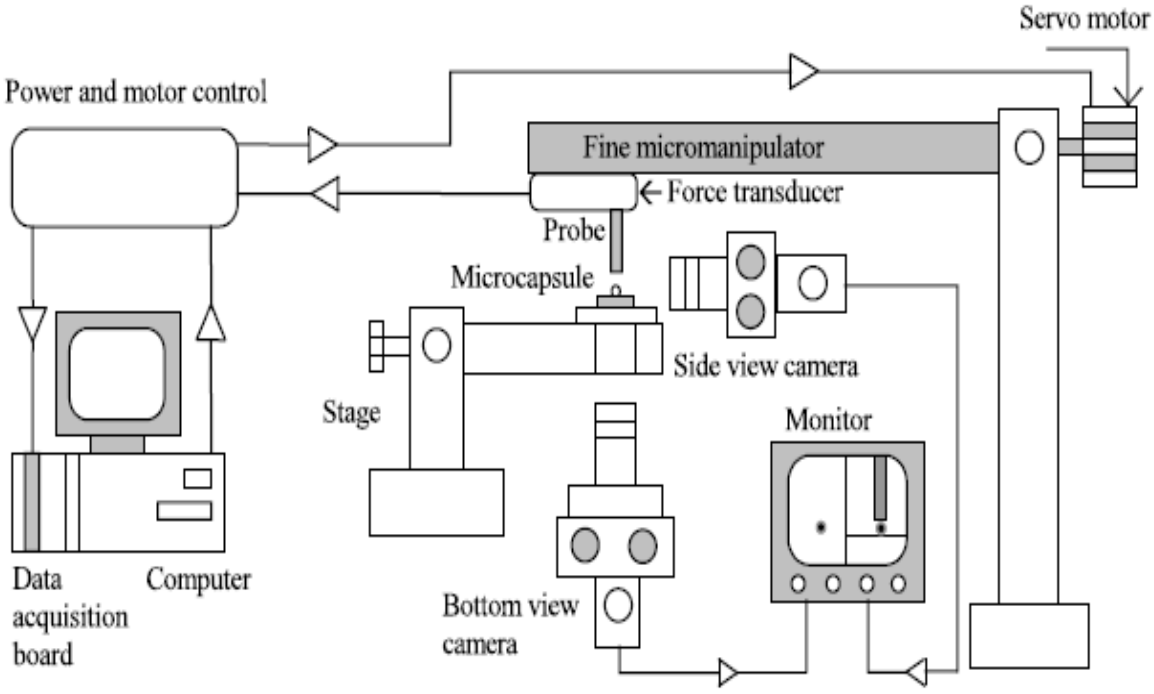


Fig. 2.40: Schematic Diagram of The Micromanipulation Rig [24]

Micromanipulation technique: the mechanical properties of melamine-formaldehyde microcapsules were determined using a micromanipulation rig, as shown in Fig. 2.40. The probe, shown in Fig.2.40, had a diameter of 50 μm and was positioned perpendicular to the bottom of a chamber. The microcapsules were dried in the chamber and observed through side-view and bottom-view cameras. Single

microcapsules compressed by the probe as it was driven downward at a given speed. Details of this technique are described elsewhere [28].

Experiments were carried out according to three stages. Firstly, single microcapsules were compressed at a speed of 1 μm/s to a certain deformation and held under the probe. Secondly, single microcapsules were compressed and released at the speed of 1 μm/s. Finally, the microcapsules were compressed up to burst at different speeds of 0.5, 1.0, 3.0 and 6.0 1 μm/s. During all these operations, the force being imposed on the microcapsules measured simultaneously by a force transducer (Model 403A, Auora Scientific Inc., Canada).

Compress and hold: Fig. 2.41 shows the force versus sample time as a M-F microcapsule was compressed to different deformations, and held afterwards. Curve a'a corresponds to the probe moving in air, ab to the microcapsule being compressed, bc to the deformed microcapsule being held under the probe. Clearly, the force being imposed on the microcapsule increased when it was deformed, and decreased gradually when it was held. The larger the final deformation, the greater the corresponding force being imposed on the microcapsule, as expected. Such results indicate that microcapsules exhibited a visco-elastic behavior.

Compress and release: Fig. 2.42 presents typical relationships between the force and displacement when single M-F microcapsules were compressed and released at 1 μm/s. As demonstrated in figure Fig. 2.42 (a), only a marginal hysteresis was found when the microcapsules had a small deformation (12% in this case). The force being imposed on the microcapsules dropped to zero only when the probe returned to its original position. Therefore, the microcapsules can be considered to be visco-elastic for such small deformations, which is consistent with the experimental results of "compress and hold". However, when the microcapsules underwent a relatively large deformation (39% in this case), there was a more profound hysteresis, and the force had already reduced to zero even if the probe was still far away from its original position (Fig. 2.42 (b)). This indicates that the microcapsules had a permanent (plastic) deformation after the force on them was completely released.

Since the microcapsules were visco-elastic at small deformations, and were plastic at relative large deformations, there may be a yield point at which the plastic behavior began to occur. As shown in Fig. 2.42 (b), the shape of the loading curve changed

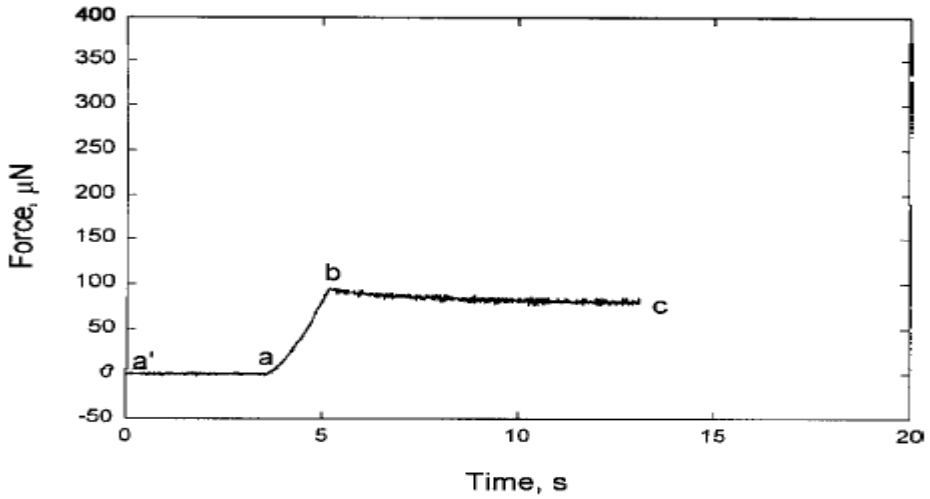
from concave to convex at point B, which may be defined as a pseudo "yield point". Mathematically, the pseudo "yield point" may be determined by the following equation:

$$d^2F / dh^2 \,|_{\text{at pseudo yield point}} = 0 \qquad (2.5)$$

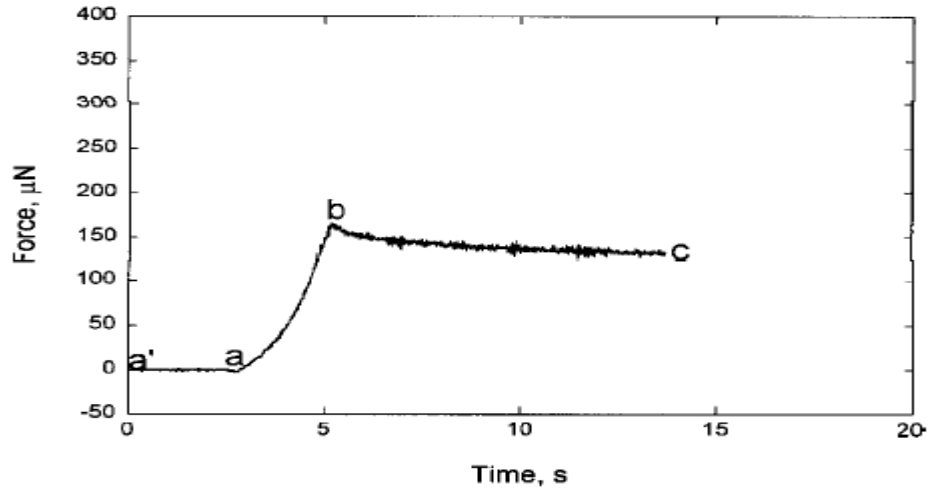
(Rektorys 1969), where F is the force and h is the displacement.

Compress microcapsules to burst: Fig.2.41 presents the relationship between the force and the probe moving distance for compressing a single microcapsule to burst. Corresponding to the curve A'A, the probe moved in air. At point A, the probe began touch the microcapsule. The force increased as the microcapsule was compressed (curve ABC). At point C, the microcapsule was burst. Then, the force soon dropped to zero and the probe was still moving until it hit the bottom of the chamber when the force began to increase sharply. The force versus displacement corresponding to the curve ABC in Fig. 2.41 is shown in Fig.2.43. Similar to Fig.2.42 (b), there exists a pseudo "yield point" (point B) on the curve in Fig.2.41 and Fig.2.43.

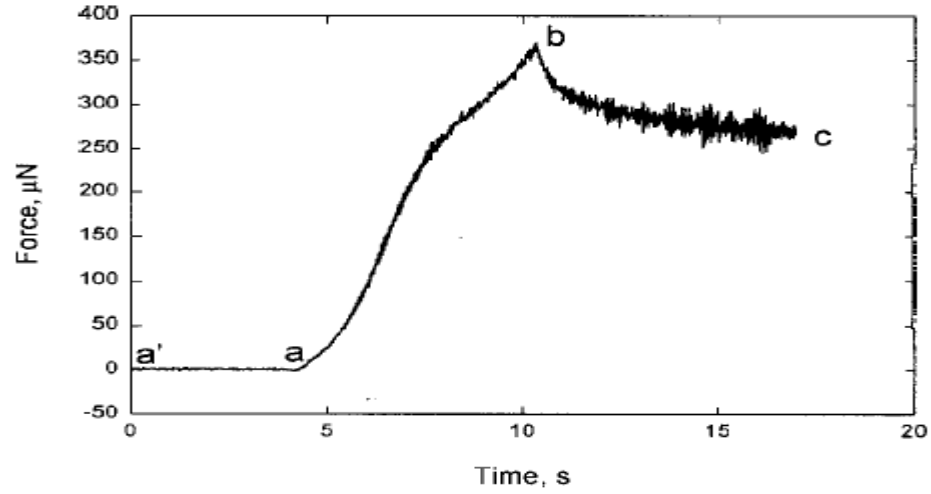
Deformation at pseudo yield point, at bursting and bursting force: Fig.2.44 and Fig. 2.46 show the displacement at the pseudo yield point, at bursting and bursting force of microcapsules versus their diameter as they were compressed at a speed of 3 μm/s. On average, the displacements at the pseudo yield point, at bursting, and bursting force of the microcapsules increased with their diameter. Their relationships are approximated by a linear regression through the origin in Fig.2.44 and Fig. 2.46.



(a) Final deformation = 11%



(b) Final deformation = 17%



(c) Final deformation = 40%

Fig. 2.41: Force Versus Time as a Single M-F Microcapsule was Compressed and Held. Microcapsule Diameter = 15 µm and Compression Speed = 1 µm/s [24].

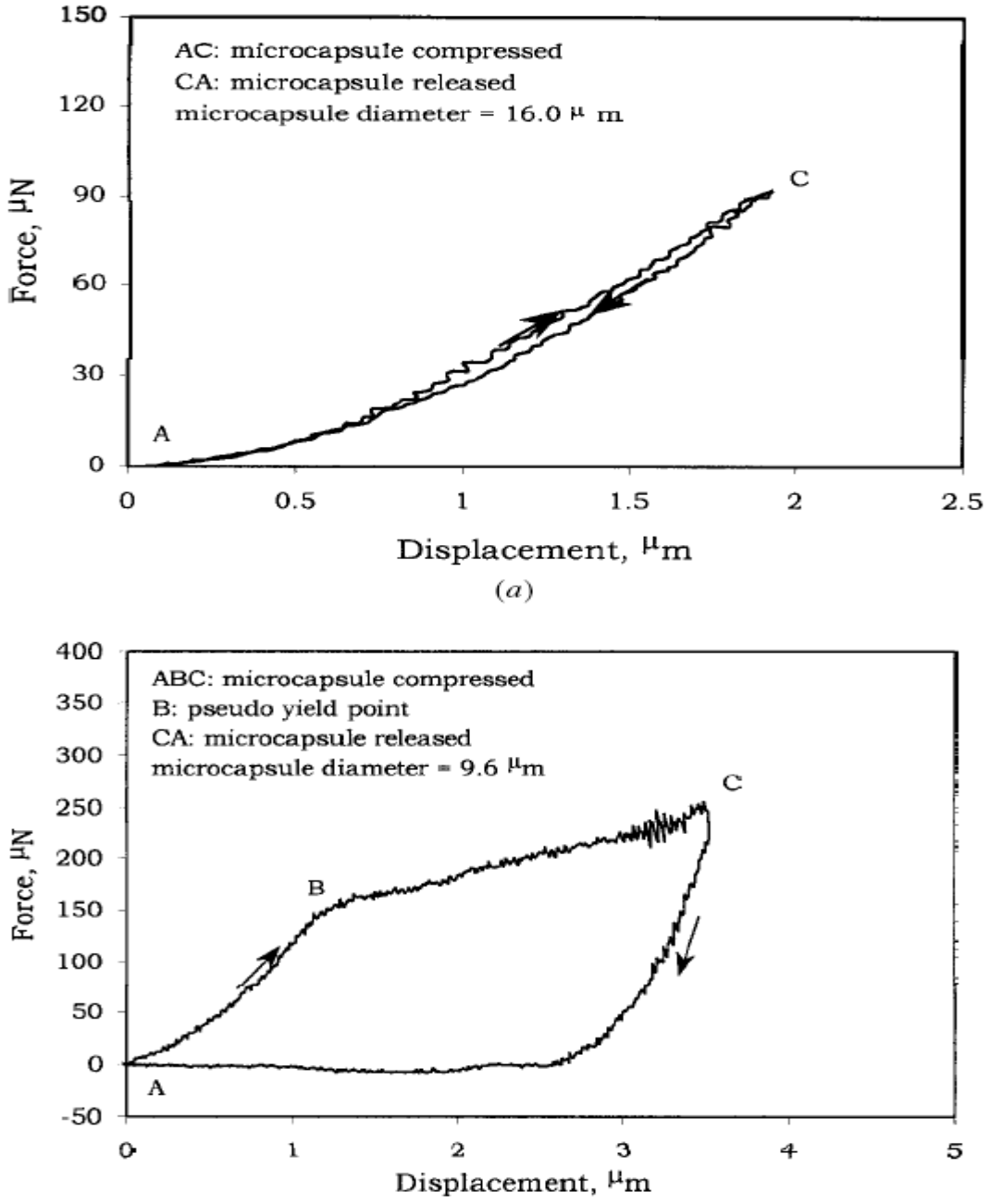


Fig. 2.42: Force vs. Displacement as Single M-F Microcapsules was Compressed and Released [24]

Similar relationships between the displacements at the pseudo yield point, at the bursting and bursting force of microcapsules and their diameter were found when the microcapsules were compressed at the speed of 0.5, 1 and 6 μm/s. If their relationships are expressed by

$$y=Kx \tag{2}$$

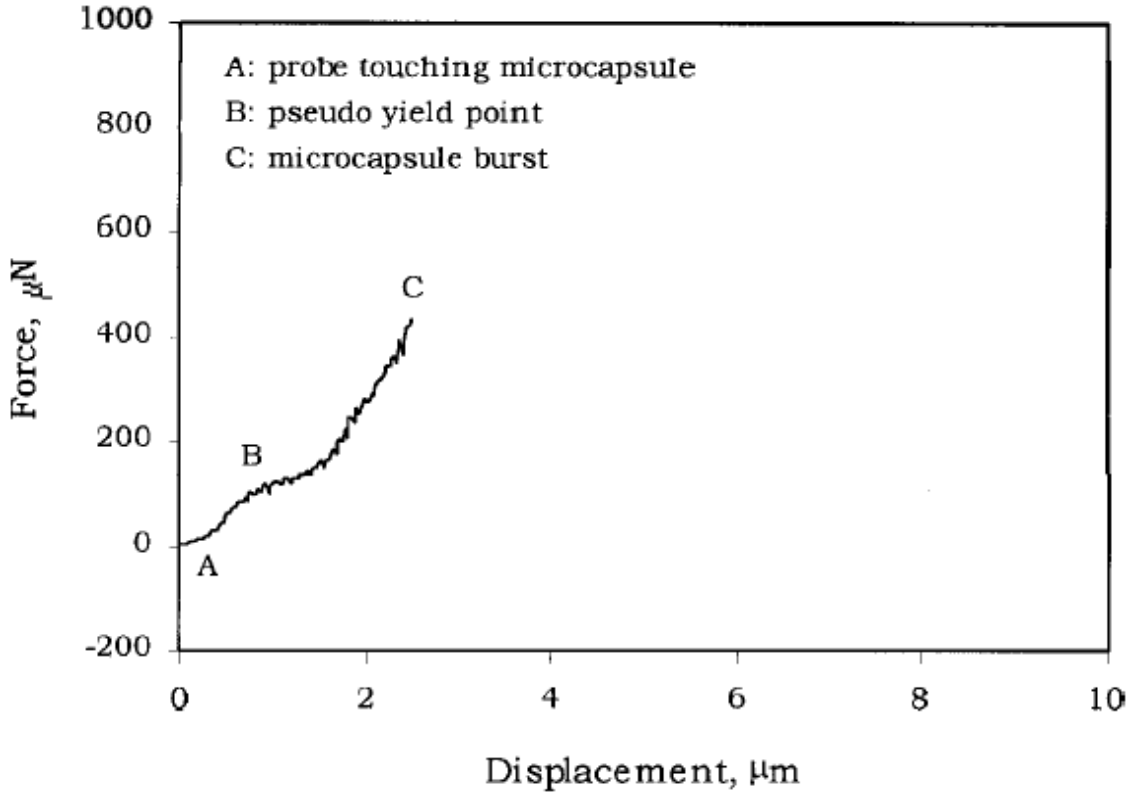


Fig. 2.43. Force versus displacement corresponding to curve ABC

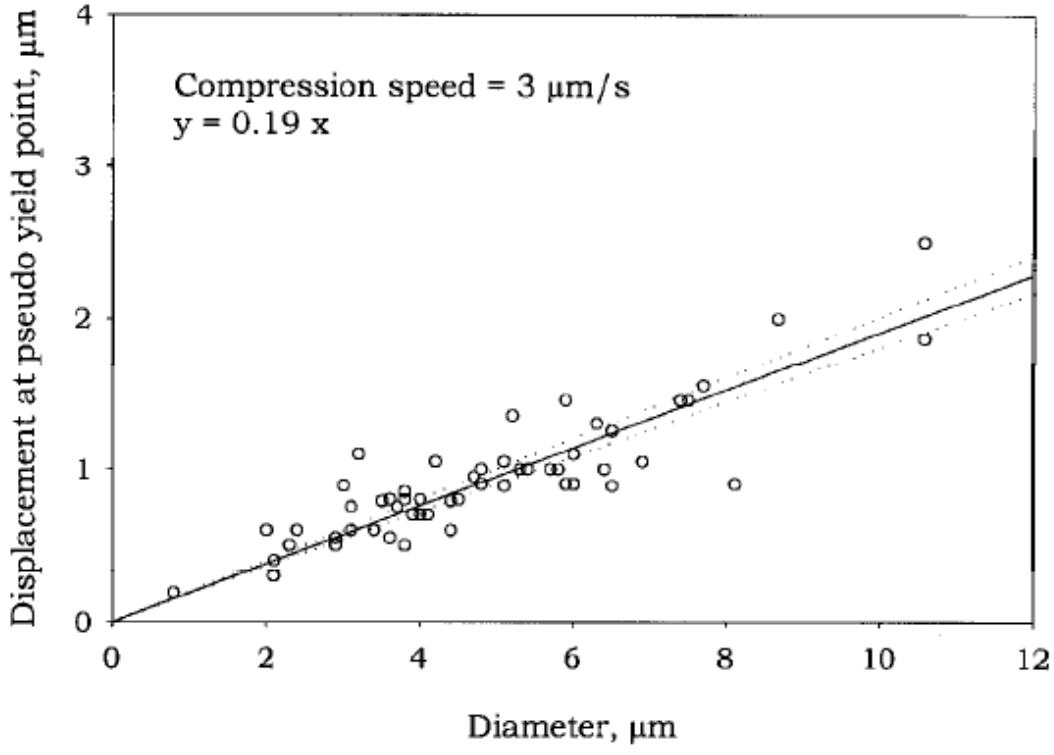


Fig. 2.44: Displacement at The Pseudo "Yield Point" Versus Diameter for Single M-F Microcapsules. Dotted Lines Represent the 95% Confidence Intervals of The Slope [24]

where y represents each of the former three parameters and x is the diameter, the K values and the 95% confidence intervals obtained at these different speeds are presented in Table 2.9.

As shown in Table 2.9 the K values do not vary significantly with the compression speed within the experimental range. On average, melamine-formaldehyde microcapsules reached their yield point at the deformation of 19± 1%, were burst at the deformation of 70±1%, and the K value for correlating the bursting force and diameter was 148± 6 μN (μm) $^{-1}$.

Table 2.9: K Values Including 95% Confidence Intervals Under Different Compression Speeds [24]

Compression Speeds (μm/s)	Number of samples	K for displacement at yield point (μm/μm)	K for displacement at bursting (μm/μm)	K for bursting force (μN/μm)
0,5	34	0,17 ±0,01	0,68 ±0,02	142 ±8
1,0	33	0,19 ±0,01	0,68 ±0,02	152 ±18
3,0	58	0,19 ±0,01	0,70 ±0,02	146 ±14
6,0	57	0,19 ±0,01	0,71 ±0,02	149 ±8
Average		0,19 ±0,01	0,70 ±0,01	148 ±6

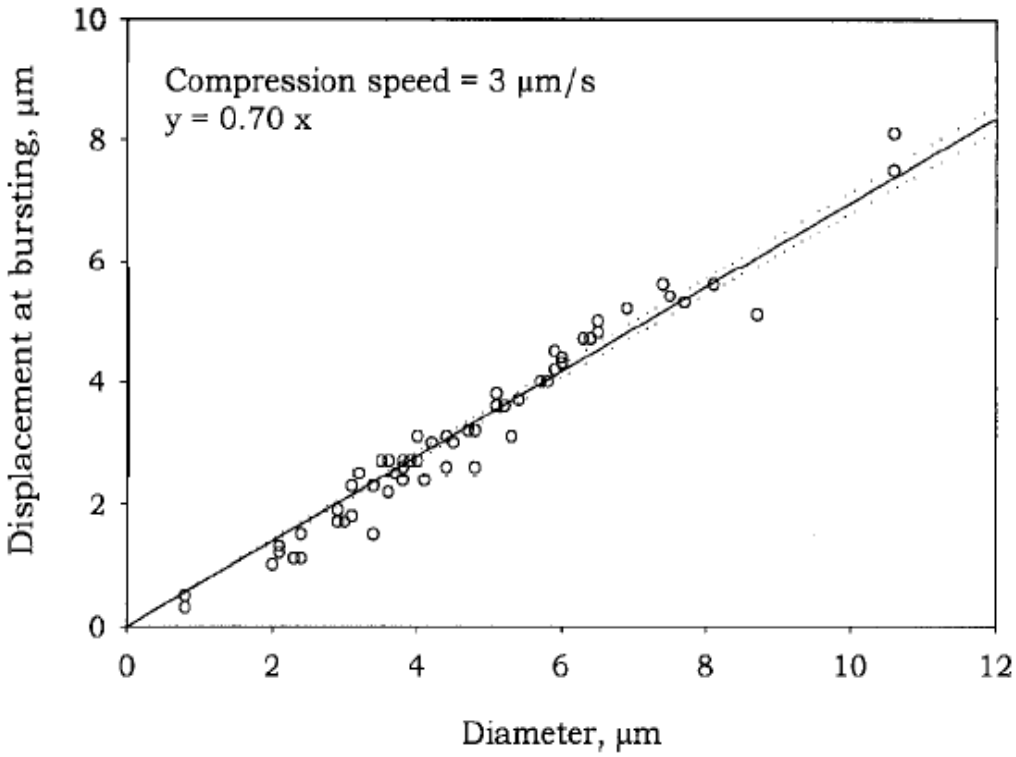


Fig. 2.45: Displacement at Bursting Versus Diameter for Single M-F Microcapsules. Dotted Lines Represent The 95% Confidence Intervals of The Slope[24]

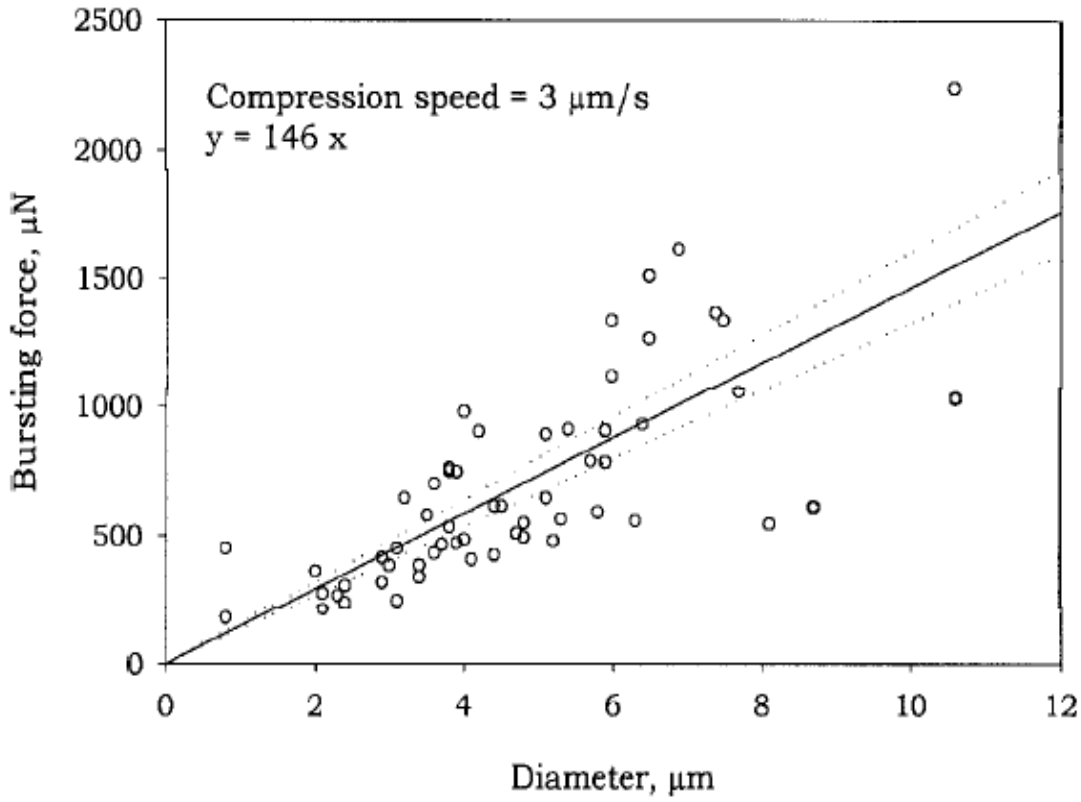


Fig. 2.46: Bursting Force Versus Diameter for Single M-F Microcapsules. Dotted Lines Represent The 95% Confidence Intervals of The Slope [24]

The compression speed did not affect the mean deformation at the pseudo yield point, at bursting and bursting force of M-F microcapsules. This implies that the viscous effect of the microcapsules on these three parameters is not significant although it existed. These results may be explained by comparing the magnitude of the relaxation time, which may be determined from the "compression and holding" experimental results (Fig. 2.41), and typical time for compressing single microcapsules to burst. It has been estimated that the relaxation time from the data in Fig. 2.41 was about 3s [29], which is comparable to the typical time for compressing single microcapsules to burst (~0.2 – 20s).

The bursting forces of the M-F microcapsules prepared for this work (K=147 μN $(\mu m)^{-1}$) were significantly greater than those in a previous report (K= 35 - 47 μN $(\mu m)^{-1}$ [28]. This is because the current M-F microcapsules had a much ticker wall (the amount of the wall material used was 50% of the core materials in weight, compared with 15-20% for the previous samples). The deformations at bursting of the microcapsules made of different wall thickness were very similar [28].

The relationship between the force and displacement for compressing single microcapsules as shown in Fig. 2.43 may be modeled to determine other mechanical property parameters, such as Young's modulus [30] and yield stress [31], by using appropriate constitutive equations (elastic, visco-elastic or plastic) of the material. The experimental results from this work have demonstrated that no simple constitutive equation can be applied to the whole range of deformation, and provided a valuable guidance to choose appropriate constitutive equations for the modeling.

The mechanical properties of melamine-formaldehyde microcapsules were determined by a micromanipulation technique. It has been found that the microcapsules exhibited a pseudo yield point under compression. Before being compressed to this point, these M-F microcapsules showed a visco-elastic behavior, but after this point the microcapsules showed plastic characteristics. However, compression speed had no significant effect on the deformation at the pseudo yield point, at bursting and bursting force. On average, M-F microcapsules reached their pseudo yield point when their deformation was 19± 1%, and burst at the deformation of 70± 1%. It is believed that such information can help to determine the stress-strain relationship from the micromanipulation measurement by using appropriate constitutive equations of the material, and predict the rupture behavior of M-F microcapsules when they are used for making carbonless copy paper or other pressure-sensitive products.

2.5.2 Mechanical strength of microcapsules made of different wall materials

After examining "The mechanical properties of melamine-formaldehyde (MF) microcapsules", G.Sun, Z. Zhang [32] made another research in the same subject and the mechanical strength of microcapsules made of three different wall materials, including melamine-formaldehyde resin, urea-formaldehyde resin and gelatin-gum arabic coacervate, were measured by a micromanipulation technique. Single microcapsules were compressed to large deformations or rupture and the being imposed on them were measured simultaneously. Melamine-formaldehyde and urea-formaldehyde microcapsules showed clear bursting under compression, and their bursting force, deformation at bursting and deformation at a pseudo yield point were determined. Gelatin microcapsules did not show clear bursting under compression,

and the force required to cause their deformation to 50% characterized their mechanical strength.

Melamine-formaldehyde (MF) and urea formaldehyde (UF) microcapsules were prepared by in situ polymerization. The amount of MF wall materials used was 50% of the core materials in weight, and that of UF was 42%. Gelatin microcapsules were made by complex coacervation.

MF and UF microcapsules were dried before their mechanical properties including strengths were determined. When single MF and UF microcapsules were compressed and held, the force imposed on them increased when they were compressed and decreased slightly when they were held. When both types of microcapsules were compressed to a small deformation and then released, e.g. 12%
(ratio of the microcapsules displacement to original diameter) for MF and 15% for UF microcapsules, there was only marginal hysteresis found from the force versus displacement curve. The force being imposed on the microcapsules dropped to zero only when the force probe returned to its original position. Therefore, MF and UF microcapsules can be considered to be visco-elastic (mainly elastic) for such small deformations, which is consistent with the experimental results of "compress and hold". However, when their deformation was relatively large, e.g. 39% for MF (Fig.2.47 (a)) and 29% for UF microcapsules (Fig. 2.47 (b)), there was a more profound hysteresis, and the force corresponding to unloading had already reduced to zero even if the force probe was still far away from its original position. This indicates that the microcapsules had permanent (plastic) deformation after the force on them was completely released. Since MF and UF microcapsules were visco-elastic (mainly elastic) at small deformations and plastic at relatively large deformations, there was a pseudo yield point at which the plastic behavior began to occur. For MF microcapsules, the deformation corresponding to this yield points was found to be at 19±1% [33], and for UF microcapsules, the deformation was 17±1%.

Gelatin microcapsules were in water suspension when their mechanical properties were characterized; since their wall appeared to collapse and core materials were released after they were dried, indicating that their wall was highly permeable to the core material. When single gelatin capsules were compressed and held, the force imposed on them increased first and then decreased slightly. When the microcapsules were compressed to a deformation of up to 50% and released, there was no

significant hysteresis observed. This indicates that gelatin microcapsules were mainly elastic up to this deformation. The drop in force being imposed on the microcapsules when they were held might be due to the loss in core materials from the wall.

Understanding of these elastic, visco-elastic or plastic behaviors of single microcapsules is essential to determination of the constitutive equations of the materials. Furthermore, the intrinsic mechanical property parameters of the microcapsules, such as Young's modulus, Poisson ratio, relaxation time, yield stress, etc. May be determined by mathematical modeling and micromanipulation measurements.

When MF microcapsules were compressed to a deformation around 68±1% they exhibited a clear bursting, represented by point "C" in Fig. 2.48 (a). Under compression UF microcapsules also showed a clear bursting, represented by point "B" in Fig. 2.48 (b), where the core material was observed to be released. In addition, after UF microcapsules were ruptured further compression resulted in cracking and yielding of the ruptured wall, which is reflected by the second peak in Fig. 2.48 (b), point "C".

On average, the bursting force and deformation at bursting of UF microcapsules increased proportionally with their diameter, as shown in Fig. 2.49. Similar results have been obtained for MF microcapsules (Sun and Zhang, 2001). However, the UF microcapsules burst when they were deformed by only 35±1%, much smaller compared with 68±1% for MF microcapsules (Sun and Zhang, 2001). The mean bursting force of UF microcapsules, Fig 2.49 (a), was also significantly smaller than that of MF microcapsules for the same size.

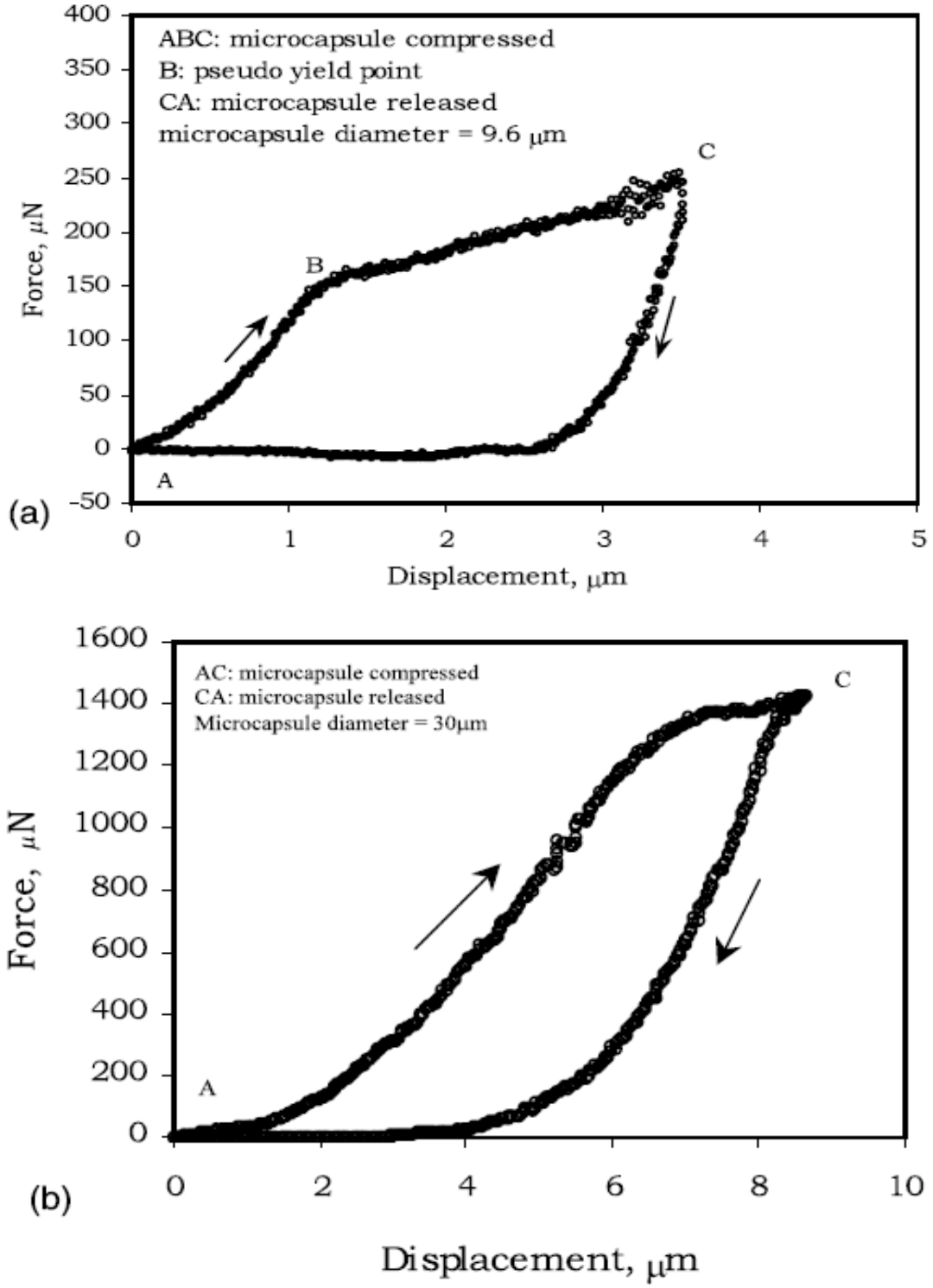


Fig 2.47: Force vs. Displacement Curve When Single Microcapsules were Compressed to a Relatively Large Deformation and Then Released. The Compression Speed was 1 μm/s. (a) MF Microcapsule; (b) UF Microcapsule [32]

Gelatin microcapsules did not show a clear rupture under compression. The force required to deform this type of microcapsules is much smaller than that of MF and UF microcapsules with same diameters. It is believed that when gelatin microcapsules were compressed the core materials were quickly released, thus

significantly reducing the pressure inside. The force required to cause 50% deformation of single gelatin microcapsules appeared to increase proportionally with their diameter, as shown in Fig. 2.50.

In conclusion, the mechanical strength of microcapsules with three different wall materials was measured by a micromanipulation technique. MF and UF microcapsules showed visco-elastic (mainly elastic) behaviors at small deformations and plastic beyond a yield point corresponding a deformation of 19±1% and 17±1% respectively. They both burst under compression, and the deformation at bursting were 68±1% and 35±1%, respectively. Gelatin microcapsules showed an elastic behavior, and did not burst under compression. This may be due to that the wall of gelatin-gum arabic coacervate was highly permeable to the core material. The bursting force and deformation at bursting for both MF and UF microcapsules increased proportionally with their diameter. The force required causing gelatin microcapsules to deform by 50% also increased with their diameter. It is believed that these results can be used to understand better the functions of the microcapsules in industrial applications or to modify their formulation in order to optimize their mechanical strengths.

In the below Table 2.10, a summary is given of the study of G.Sun, Z. Zhang.

Table 2.10: Summary of The Study of G.Sun, Z. Zhang

Condition	Result	Reason
MF resin, UF resin and Gelatin-gum arabic coacervate as shell material of microcapsule is used.	Melamine-formaldehyde and urea-formaldehyde microcapsules showed a clear bursting. Gelatin microcapsules did not show a clear bursting under compression. The best option is to use MF resin.	Because, UF microcapsules burst when they deformed only 35%, while MF microcapsules bursted after 68% deformation. So, MF capsules have more visco-elastic behavior tendency.
The higher the diameter, the higher the bursting force is required	MF microcapsules are more resistant than that of UF and gelatin capsules.	Because, gelatin microcapsules deformation changes start after 50% shape change while, respectively, 35% for UF microcapsules and 68% for MF capsules

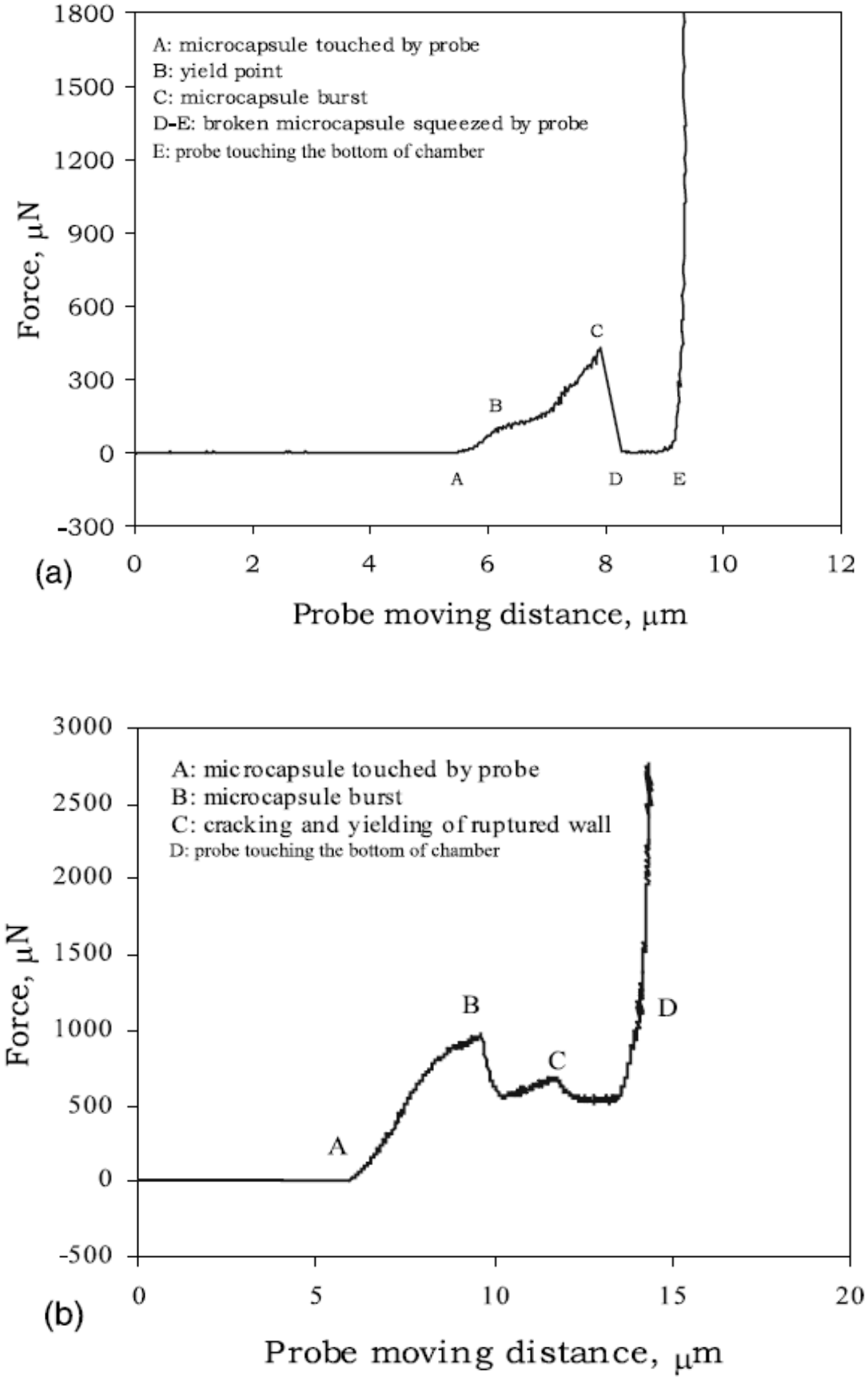


Fig. 2.48: Force Versus Probe Moving Distance for Compressing Single Microcapsules to Rupture. (a) MF Microcapsules; (b) UF Microcapsules [32]

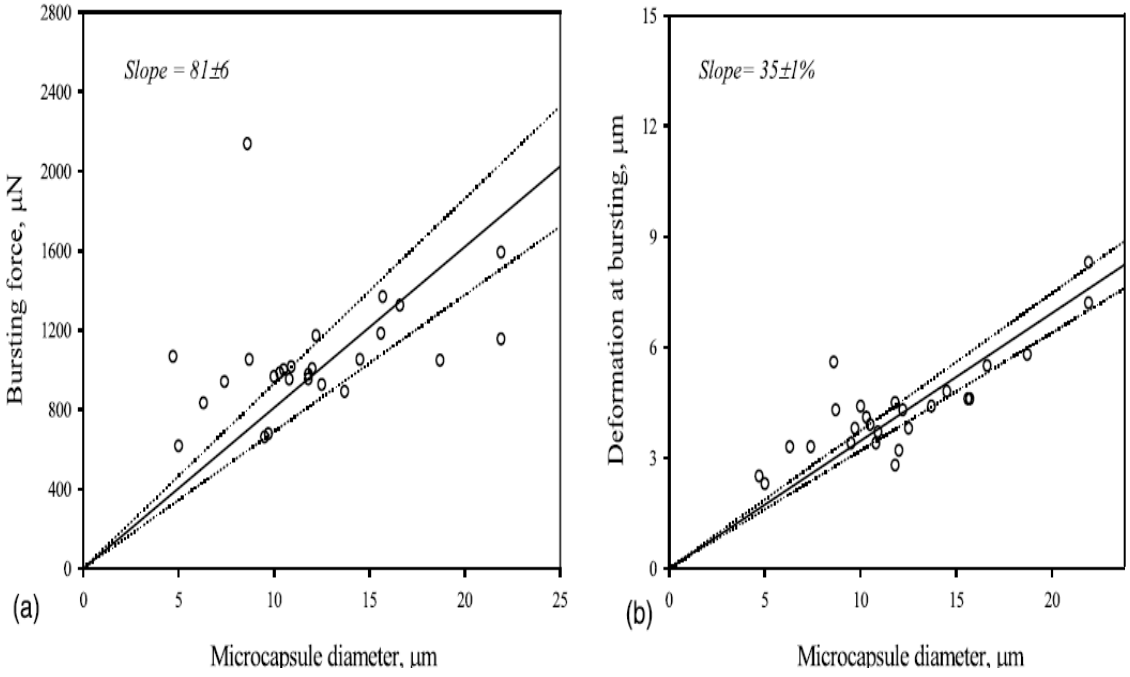


Fig. 2.49: Bursting Force (a) and Deformation at Bursting (b) vs. Diameter for UF Microcapsules. The Compression Speed was 1 µm/s. The Solid Lines in Figs. 2.5.2.2 and 2.5.2.3 Represent The Linear Regression Passing Through The Origin, and The Dash Lines Show The 95% Confidence Limit of The Regression [32]

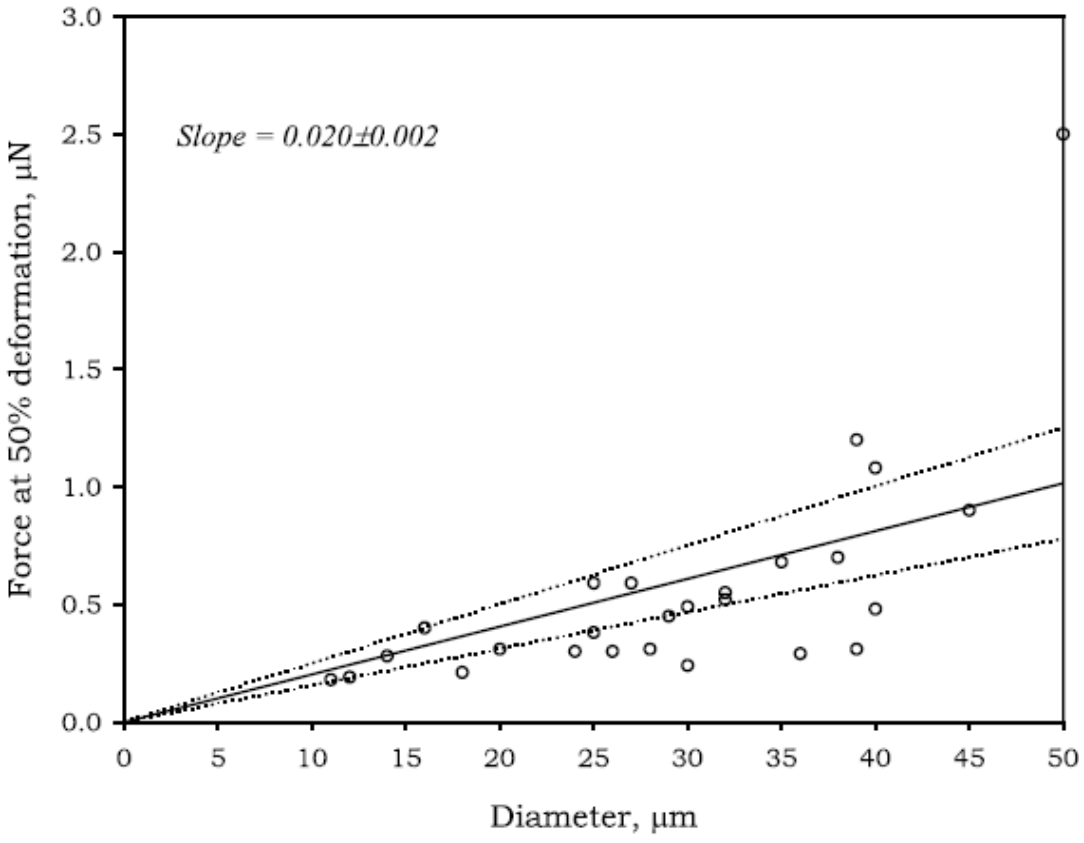


Fig 2.50: Force Required to Cause 50% Deformation Versus Diameter for Gelatin Microcapsules. The Compression Speed was 1 µm/s. [32]

2.6. Properties of Chitin and Chitosan Polymers

Cellulose is a bio-molecule that presents in the cell walls of plants, trees, seaweed, etc. It is the most abundant biopolymer on earth [34].

Chitin, which is the second most abundant biopolymer in the world. Curiously, the molecular structure of chitin is almost identical to cellulose (Fig. 2.51), except for the replacement of hydroxyl group on each monomer of cellulose, with an acetyl amino group in chitin. Chitin thus contains nitrogen, which cellulose doesn't and this provides new opportunities for example in binding metals.

Chitin is found as a structural polymer in the tough exoskeletons of invertebrate arthropods such as insects and in the shells of crustacea (crabs, lobster and prawn) (Fig. 2.52). Chitin is also the main structural polymer of the cell walls of fungi. Because of the molecular similarity of the two structural biopolymers they, in all probability, have similar biogenetic roots.

Fig.2.51: Chitin Source [34]

Both of these renewable materials are polysaccharides with a host of diverse and valuable end-uses. Nevertheless, while the application of cellulose to paper -making, biodegradable polymers ('Rayon', cellulose acetate) etc. is widely known, the new and exciting end-uses for chitin and chitin-like molecules have not as yet really reached the public eye. Until only a few years ago, hundreds of thousands of tones of chitin-rich waste in the form of prawn, crab, and langoustine and shrimp shell were disposed of in landfill or at sea, at great cost to the processor. Now, the true value of these renewable materials is being realized and capitalized, and much of this waste is being processed to extract the valuable chitin polymer.

Chitin itself (like cellulose) is insoluble in water, but can be easily modified by either conventional chemistry or preferably a green chemistry route to form chitosans, which are a family of chitin-related molecules having varying degrees of solubility. In addition, their viscosity can be controlled to form very low viscosity species through to stiff gels. These properties along with their unique chemistry make chitosans very versatile in terms of what we can use them for. Some interesting examples of end uses from the growing list of applications include**:**

Manufacture of Membranes: Because of hydrogen bindings of the chitosan polymers (due to the acetyl amino groups), they can be cast into very thin stable sheets and formed into strong membranous structures. These thin, flexible, biodegradable sheets have very broad industrial application including microencapsulation (used for the controlled release e.g. enzymes, drugs, fertilizers etc.) [34].

Chitosan formed into membranes can be used in water softening by virtue of their calcium-chelating properties; the biocidal properties of the molecule are also advantageous to this application.

Due to the anti-microbial properties of the polymer, chitosan formed into films can be used in packaging, which thus retards putrefaction and aids preservation.

Fat Binding: Chitosan is oleophilic (oil-loving) and has been used to encapsulate fatty foods in the gut and thus slows their enzymatic breakdown and subsequent rate of absorption. They are thus useful dietary ‘fat busters’.

Personal Care Products: Soluble chitosans can be used in hair care applications due to their setting and conditioning properties. Because of their high water-binding capacity, chitosans are valuable addition to emollients and moisturizers in skin-care applications. They also form protective layers across the skin, which increases subcutaneous moisture content [34].

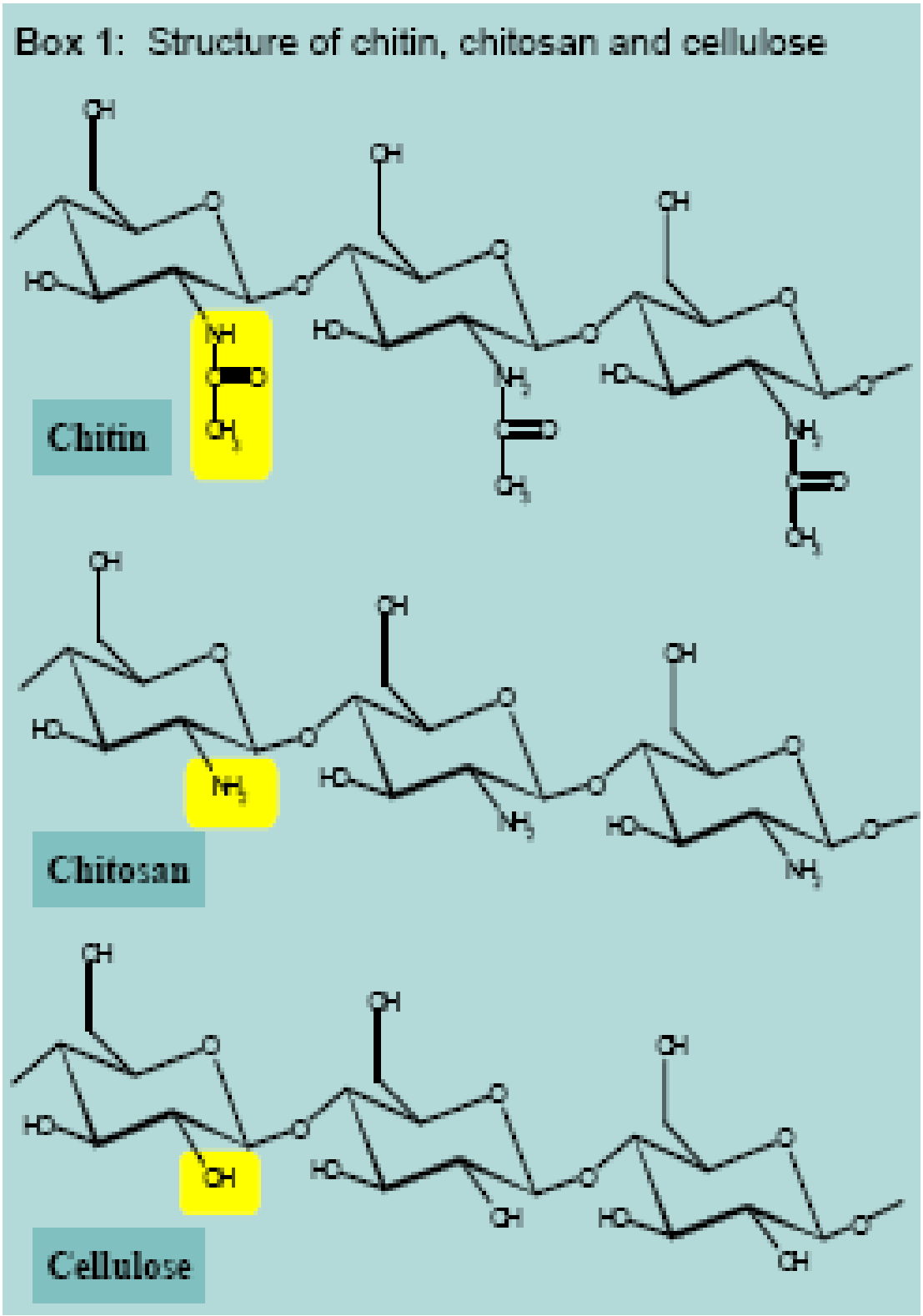


Fig. 2.52: Formulas of Chitin, Chitosan and Cellulose [34]

The degree of acetylation: the degree of acetylation is one of the most important structural parameters in chitin and chitosan [35]. Many methods have been developed for analyzing the degree of acetylation, ranging from elemental analysis,

infrared spectroscopy, colloidal titration, circular dichroism, ultraviolet spectroscopy following the method of Muzarrelli et al., pyrolysis–gas chromatography, gel permeation chromatography and thermal analysis, acid hydrolysis and HPLC to ^{13}C-NMR, ^{1}H- NMR (nuclear magnetic resonance) [100] and X-ray diffraction methods. There are two advantages of chitosan over chitin. In order to dissolve chitin, highly toxic co solvents such as lithium chloride and dimethylacetamide must be used whereas chitosan is readily dissolved in agents such as 1-10% (v/v) aqueous acetic acid. The second advantage of chitosan is the presence of the free amine group that not only renders polyelectrolytic to the polymer backbone, but also presents an active site upon which many chemical reactions may be applied.

Chitin and chitosan polymers could be made on form of monofilament fibers, films, tubes, straws, capsules, nonwoven fabric, sponge, powder and gel forms, etc.

Production methods and their parameters: in the most studies, chitin and chitosan fibers produced by a wet-spinning process, but rarely by a dry-spinning process. When using wet-spinning process to produce fibers, the two polymers firstly are dissolved in a solvent and then the polymer solution is extruded via fine holes (especially through a viscose-type spinneret into a non-solvent (coagulant) at 45-50 °C. The polymer precipitates out in the form of a filament, which can be washed, drawn, and dried to form the fibers.

Chitin and chitosan and their derivatives have various potential application fields ranging from flocculants for waste-water treatment, seed coating, toiletry components, additives for shampoos and cosmetics and drug deliveries to eye contact lens, digestible sutures, dietary fibers, wound-healing dressing material (artificial skin), antimicrobial agents, various medical suppliers including sanitary cottons, gauzes, bandages, plasters, sanitary pads and cotton swabs, food preservatives, medicines, antifungal textile promoters for plant growth, supports for biologically active species, separation membranes, adsorbents for affinity chromatography, adsorbents for metal cations, matrix for immobilization of biomolecules, antitumour activity, applications in controlled drug release and in bio-separation, immunological applications, support for bio sensors, removing of heavy metals, removing of dyes and certain surfactants from effluents, removing of radioactive waste, etc.(Table 2.11)

Chitin and Chitosan Manufacturing Process

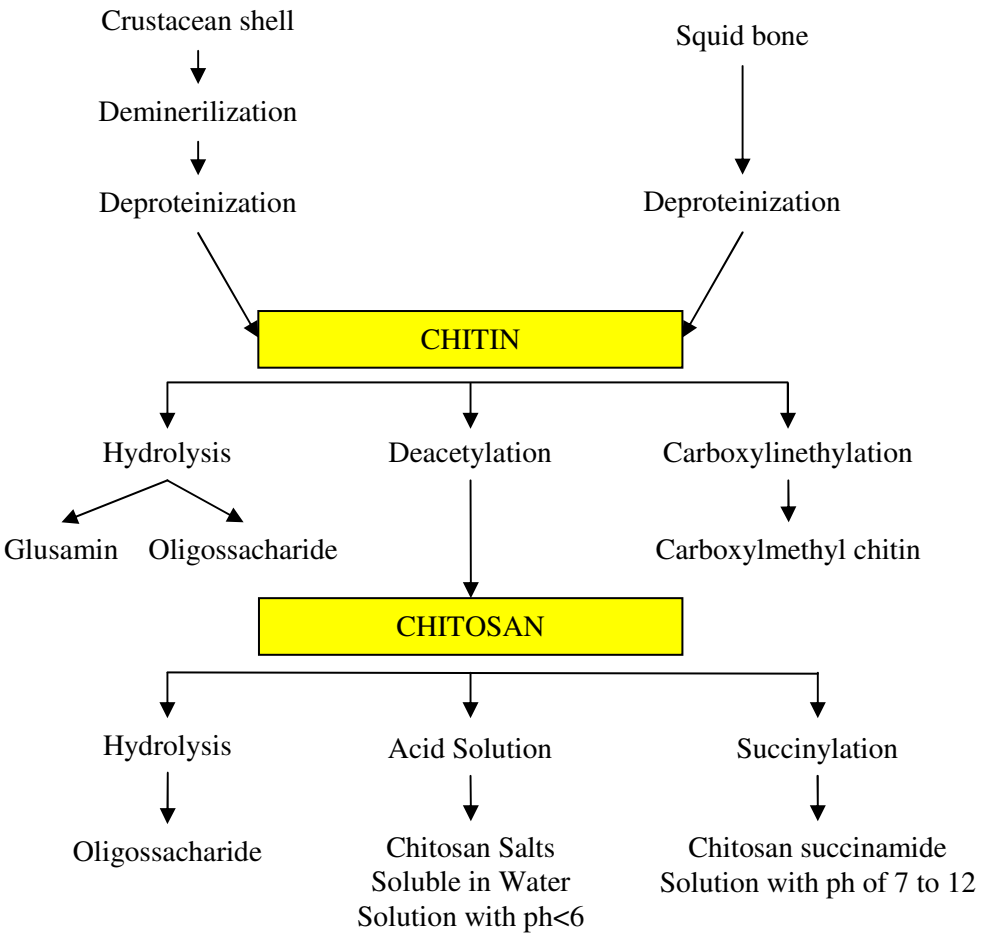


Fig.2.53: Chitin and Chitosan Manufacturing Process [35]

2.6.1. Chitosan Applications

Table 2.11: Application areas of chitosan and its derivatives [35]

Application of Chitosan	
Wastewater Treatment	Removal of Metal Ions
	Flocculant/ Coagulant
	Protein
	Dye
	Amino Acids
Food Industry	Removal of Dye, Suspended solids, etc.
	Preservative
	Colour Stabilization
Medical	Bandages
	Blood Cholestrol Control
	Controlled Release of Drugs
	Skin Burn
	Contact Lens, etc.
Agriculture	Seed Coating
	Fertilizer
	Controlled Agrochemical Release
Cosmetics	Moisturizer
	Face, Hand and Body Creams
	Bath Lotion, etc.
Biotechnology	Enzyme Immobilization
	Protein Separation
	Cell Recovery
	Chromatography
	Cell Immobilization
Pulp and Papers	Surface Treatment
	Photographic Paper
Membrane	Permeability Control
	Reverse Osmosis

2.6.1.1. Enzyme Immobilization by Chitosan

There were many reasons why chitosan was selected as a material for the microcapsule shell in the research of E. Taqieddin, M. Amiji in 2003 [36]. First, it is a second-most abundant cationic biopolymer with intra- and intermolecular hydrogen bonding ability. Various geometries such as membranes, fibers, and capsules can be easily formed from chitosan [37,38]. Second, they developed a unique approach to modify the surface of chitosan by a complexation-interpenetration of anions (e.g. heparin, dextran sulfate, and poly(ethylene glycol)- sulfonate) to improve

biocompatibility [38,39]. Surface-modified chitosan can resist protein adsorption and cell adhesion in the biological milieu. Lastly, they also developed the technology to create chitosan membranes with controlled pore size and density, such that molecules of specific size can permeate through [40].

Chitosan is a promising candidate for enzyme immobilization. It is obtained from alkaline hydrolysis of chitin, and thus, abundantly available from renewable resource. Chitosan is biocompatible and has been used in many applications including delivery systems [41]. One disadvantage of chitosan is its limited solubility in water. Chitosan requires dilute acidic solutions for dissolution. The low pH of chitosan solution tends to denature most proteins and cells, and as such, is not a suitable material for immobilization.

2.6.1.2. Potential Drug Carrier: Chitosan

Chitosan is a biodegradable natural polymer with great potential for pharmaceutical due to its biocompatibility, high charge density, non-toxicity and mucoadhesion. It has been shown that it is not only improves the dissolution of poorly soluble drugs but also exerts a significant effect on fat metabolism in the body. Gel formation can be obtained by interactions of chitosan with low molecular counterions such as polyphosphates, sulphates and cross-linking with glutaraldehyde [42].

Chitosan, a natural linear bio polyaminosaccharide is obtained by alkaline deacetylation of chitin, which is the second abundant polysaccharide next to cellulose [43].

Commercially, chitosan is available in the form of dry flakes, solution and fine powder. It has an average molecular weight ranging between 3800 and 2.000.000 and is from 66 to 95% deacetylated [45]. Particle size, density, viscosity, degree of deacetylation, and molecular weight are important characteristics of chitosan which influence the properties of pharmaceutical formulations based on chitosan.

Properties such as biodegradability, low toxicity and good biocompatibility make it suitable for use in biomedical and pharmaceutical formulations [44,46] e.g. it is used for hypobilirubianemic and hypocholesterolemic effects [47,48], antacid and antiulcer activities, immobilization of enzymes and living cell and in ophthalmology [49]. Since chitosan has a capacity of forming film it has been suggested as a

biopolymer of choice for the development of contact lens (soft and hard contact lenses). Chitosan has been used for the manufacturing ocular bandage lenses used as protective devices for acutely or chronically traumatized eyes [50]. Chitosan membranes have also been found useful as artificial kidney membranes because of their suitable permeability and high tensile strength [51].

Chitosan possesses no toxicity and can be applied onto the nasal epithelium. It swells and forms a gel like layer in aqueous environment (by absorbing water from the mucous layer in the nasal cavity), which is favorable for interpenetration of polymer and glycoprotein chains into mucous [52].

2.6.1.3. Pharmaceutical Applications

Among pharmaceutical applications it has been used as a vehicle for directly compressed tablets [53-55], as a disintegrant [56], as a binder [57], as a granulating agent [58], in ground mixtures [59], as a drug carrier for sustained release preparations [60-63] as well as a co-grinding diluents for the enhancement of dissolution rate and bio-availability of water insoluble drugs [64-66].

2.6.1.4. Mucoadhesive Applications

Chitosan has been shown to possess mucoadhesive properties [67-72] due to molecular attractive forces formed by electrostatic interaction between positively charged chitosan and negatively charged mucosal surfaces. These properties may be attributed to:

a) Strong hydrogen bonding groups like –OH, -COOH [73]

b) Strong charges [74]

c) High molecular weight [75,76]

d) Sufficient chain flexibility [70]; and

e) Surface energy properties favoring spreading into mucus [77]

2.6.1.5. Food Industry Applications

In recent years, chitosan has been used for development of oral controlled drug delivery systems. It is also a well-known dietary food additive. Vitamin C, a representative water-soluble vitamin, has a variety of biological, pharmaceutical, and

dermatological functions. Vitamin C is widely used in various types of foods as a vitamin supplement and as an antioxidant [78]. The process of the preparation of vitamin C-encapsulated chitosan microcapsules is shown in Fig. 2.54; chitosan was cross-linked with nontoxic cross-linking agent, i.e., tripoylphosphate. Vitamin C-encapsulated chitosan micro-spheres of different size, surface morphology, loading efficiency, and zeta potential with controlled-release property could be obtained by varying the manufacturing parameters (inlet temperature, flow rate) and using the different molecular weight and concentration of chitosan. Vitamin C-encapsulated chitosan microcapsules were spherical in shape with a smooth surface as observed by scanning electron microscopy (Fig 2.55). Microencapsulation of vitamin C improves and broadens its applications in the food industry.

Numerous materials have been used as flavor-encapsulating agents using a spray-drying technique. These include proteins, gums, and modified starches [79]. An area of research of increasing interest is the development of alternative and inexpensive polymers that may be considered natural, like gum arabic, and that could encapsulate flavors with the same efficiency as gum arabic [80]. Mesquite gum has been reported as a very good encapsulating agent [81,82]. Beristan and Vernon-Carter noted that a blend of 60% gum arabic and 40% mesquite gum encapsulated 93.5% of orange peel oil [83]. More recently, Beristan et al. reported that a mixture consisting of 40% mesquite gum and 60% maltodextrins was able to encapsulate 84.6% of the starting oil [84]. Cardamom-based oil microcapsules were successfully produced by spray - drying using mesquite gum [85]. The stability against drop coalescence of the emulsions was elevated for all the gum: oil ratios studied. High flavor retention (83.6%) was attained during microencapsulation by spray- drying when a proportion of 4:1 gum: oil was used. This confirmed the interesting emulsifying properties and good flavor-encapsulation ability that qualify mesquite gum as an important alternative encapsulation medium.

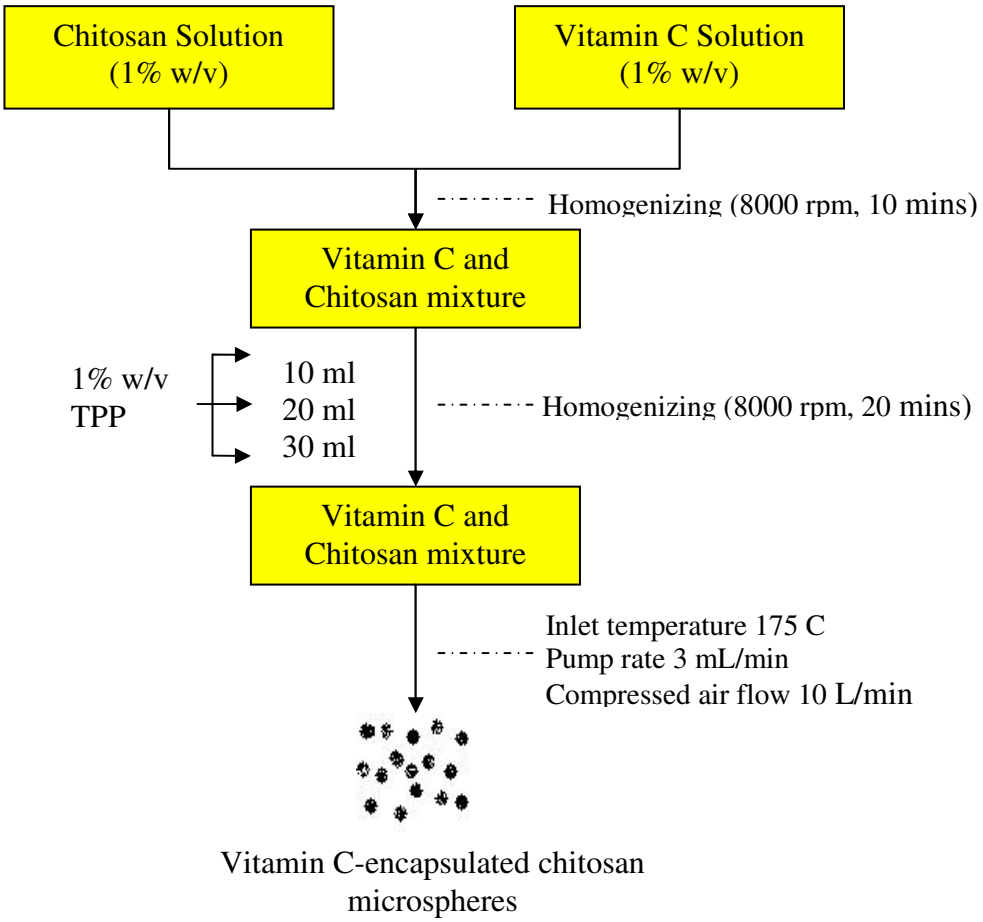


Figure 2.54: Procedure of Preparation of Vitamin C-encapsulated Chitosan Microspheres by Spray-drying [78]

The microcapsules can be readily used as a food ingredient. Recent developments have been in the use of new carrier materials and a newly designed spray dryer. Colloides Naturels and TIC Gums have developed a new combination of gum arabic starches to increase the retention of volatiles and shelf life of microcapsules [86,87]. Risch and Reineccius enhanced the retention of orange oil and decreased oxidation by using gum arabic [88].

Bhandari et al. showed that a new type of dryer called the Leaflish spray dryer, which uses a high air velocity with a temperature of 300 to 400°C, was effective for encapsulating citral and linalyl agglomeration step is required to prevent separation or to render the obtained powder soluble. A chief advantage is that this technique can be used for heat-labile materials. Recently, studies on the modification of spray-drying chamber configurations and atomization along applications of computational fluid dynamic model have been reported to broaden the applications range of spray-drying methods [89-94].

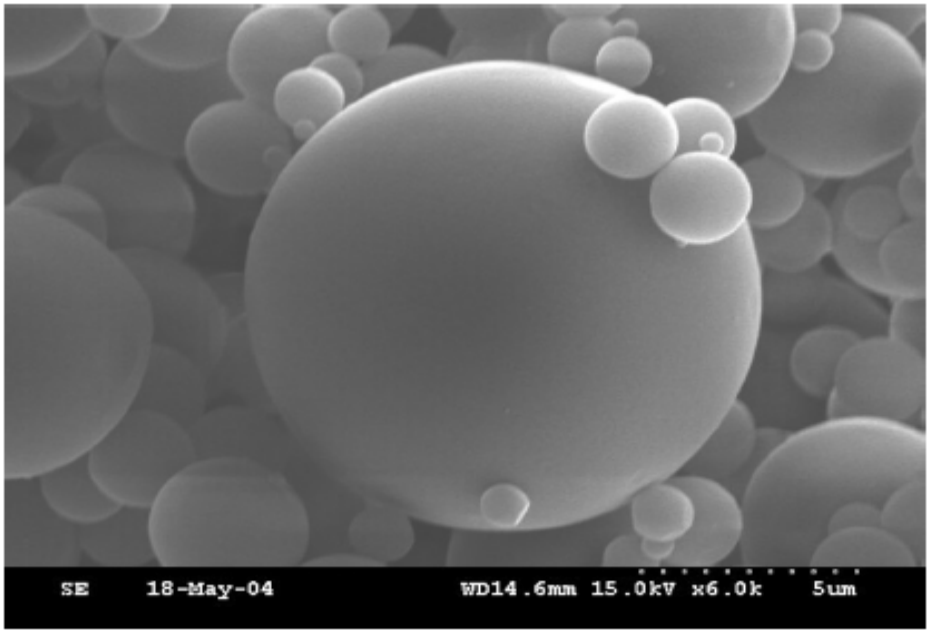


Fig. 2.55: Scanning Electron Microscopic Picture of The Vitamin C-encapsulated Microcapsule[78]

2.6.1.6 Coating Applications of Chitosan Solution

In this method, previously formed micro-particles are coated with chitosan [95-100]. Human serum albumin (HSA) micro-spheres were prepared and added to various concentrations of chitosan- acetic acid solutions and mixed. The coated micro-particles were filtered and dried.

Lin and Kang [101] coated poly (epsiloncaprolactone) (PCL) micro-particles with chitosan and gelatin. The release of indomethacin from uncoated micro-particles followed a two-exponential release profile, where indomethacin was rapidly released within 4 h during the first release phase, after that approximately 20% of the drug was released continuously and slowly up to 24 h in the second phase. The similar release profile was observed from coated micro-particles irrespective of the times of coating and the types of coating material. Both the natural coating materials, chitosan and gelatin, efficiently reduced the initial burst release in the first phase of drug release, but did not alter the second phase of drug release.

Takishima et al. [102] prepared etyhlcellulose micro particles and coated them with chitosan solution. When fluorescein isothiocyanate (FITC)-labeled chitosan-coated ethyl cellulose micro particles without drug were administered intraduodenally, they moved slowly in the intestine, that is, most of them were retained at the upper and

middle parts of the small intestine for more than 8 h, which is considered appropriate due to mucoadhesive properties of coated chitosan.

2.7. Important Parameters Which Play Active Roll in Microcapsules Release Mechanism

In recent years out of the fear of SARS, Dengeu Fever, and Avian Influenza (Bird Flu), people start to take personal hygiene, health care and other protective measures seriously. The volatile essential oils that have efficacies of antibiosis, insect repelling and stress reducing are valued by many [103-105].

The release speed of these volatile essential oils usually was affected by different application environment conditions. Thus, released too little and causes ineffectiveness, or released excessively and causes uncomfortable feelings [106-110]. Therefore how to control these volatile essential oils to have constant release in various application environment conditions is a good subject quite worth investigation and discussion. Utilizing microencapsulation technology to achieve the goal of constant release is one of the most effective methods thus far [111-113]. However at present time there is infrequent study and research related to the technology of encapsulate volatile material in microcapsules and discuss its sustained release property for application in personal hygiene and health care domain [114-116].

Therefore, providing a perfect controlled release mechanism via microencapsulation process has utmost importance in many industries as well as in textile industry. In this thesis, the parameters that directly affect the release speed of the microcapsules have been examined. And try to be find out what the best practice or practice combination is.

Textile manufacturers show more and more interest in the textile with durable odour or a cosmetic product that is released by the contact with the skin. Others applications are being studied (products against insects, colorating, vitamins, and phase change material.) The highest benefit of the microcapsules is that compared to a normal tablet in which the active ingredient is in bulk, microcapsules have much greater surface area that increases solubility and effectiveness. Microcapsules can be engineered to gradually release drugs to the body.

The uses of microcapsules that are of interest here include the following:

1- Reduce the reactivity of the core with regard to outside environment, for example oxygen and water;

2- Decrease the evaporation of transfer rate of the core material to the outside environment;

3- Promote the ease of handling of the core material;

a. Prevent lumping;

b. Position the core material more uniformity through a mix by giving it a size and outside surface like the remainder of the materials in the mix.

c. Convert a liquid to a solid form; and

d. Promote the easy mixing of the core material.

4- Control the release of the core material so as to achieve the proper delay until the right stimulus;

5- Taste mask the core; and,

6- Dilute the core material when it is only used in very small amounts; but achieve uniform dispersion in the host material.

Wall materials of microcapsules: Gelatine, starch, gum arabic, amino- formaldehyde resins, ethyl cellulose, polyurethane's, paraffin, polyamides, polyvinyl alcohol, metals, polyproylene, lipids.

Core materials of microcapsules: adhesives, food, colours, bacteria, herbicides, viruses, hardeners, monomers, pigments, drugs, vitamins, fragrances, dyes, plasticizers, enzymes & oils.

2.7.1. Controlled Release Characteristics of Citronella Oil Microcapsules

Citronella oil which posses mood lifting, depression and restless reducing, deodorizing, sterilizing, bug repelling properties as the core material [117] was searched by Wen-Chuan H, Chih-Pong C, Ying-Lin G in 2006 [118]. They used chitosan as the wall membrane material. Chitosan possesses heat shrinking property, thus by using this unique property to change the pore space between the chitosan wall membrane molecules, and achieve the controlled release effect of the content within the microcapsules [119,120]. They studied the forming and manufacturing conditions of microcapsules such as the amount of the wall membrane material added, the concentration of cross-linking agent, the emulsification stirring speed, the

thermal treatment temperature and treatment time, and their influence to the effect of sustained release of the volatile citronella oil.

First added 0.5 wt% yellow oily dye in the citronella oil for tracing purpose; then poured 2 ml of the yellow citronella oil into 20 ml of solutions consisting of 0.2%, 0.5%, 1.0% and 1.5%chitosan, respectively; using homogenizer (HG-300D+ K12S, Shuang-Tai, Taiwan) to stir 10 min in 400-1.500 rpm speed that cause the intermixture emulsification; then dripped in 0.1-1.5 wt% NaOH while stirring slowly. Thus formed the chitosan wall membrane on the surface of the citronella oil particles and created the microcapsule sample. After washing the microcapsules samples with distilled water twice and then dislodge other unwanted substances with a centrifuge, then placed into 5wt % natural coconut oil amphoteric surfactant solution for 10 days. The resultant chitosan microcapsules samples were dried in a vacuum oven (TK30, Young-Chen, Taiwan) at 30 °C overnight to evaporate any remaining water on the microcapsule surface. The sample weight was then measured and defined as W_m. Then observed the formation and dispersion of the microcapsules afterward under optical microscope.

Determination of microcapsule size: the particle sizes of the prepared microcapsules were determined by using particle diameter and particle size analyzers (MSS, Malvern Instruments, UK). The sizes of the microcapsules were determined in chloroform as a non-dissolving dispersion medium and the particles were mechanically suspended by magnetic stirring during the measurement.

Determination of controlled release and data analysis: the release of citronella oil from the microcapsules at the incubation process was estimated by measuring the time course of the weight W_m (t) of the microcapsules placed in an Infrared Moisture Determination Balance (IMDB) (AD-4715, AND) at 40 °C. Here, t is the incubation time. Even tiny amount of vaporization of solvent could be detected by IMDB, as it is commonly used to determine the water content of fibers. The sample in the open box of IMDB was heated by using infrared set at desired temperatures. Temperature and weight of the sample were measured continuously and recorded automatically. The oil release content was defined as:

$$\psi\ (\%) = [[W_m - W_m(t)] / [W_m - W_o]] \times 100 \qquad (2.6)$$

Where W_o denote the weight of microcapsules measured after complete evaporation of citronella oil at 120 °C for 3 h. Therefore, the encapsulation efficiency can be defined as:

$$\varphi\ (\%) = [(W_m - W_o) / W_m] \times 100 \qquad (2.7)$$

The citronella oil release curves were expressed by the exponential equation:

$$\psi\ (\%) = C_{eq}\ (1\text{-}e^{-t/\tau}) \qquad (2.8)$$

Where ψ (t) represents the variant of citronella oil concentration in the operation environment, C_{eq} the equilibrium state, t the release time and τ is time constant. Thus τ is the significant factor pertaining to the citronella oil release properties.

The formation and encapsulation efficiency of microcapsules: in order to discuss the optimum formation condition of the microcapsules, the change factors that were used are the concentration of chitosan in 0.2wt %, 0.5wt %, 1.0wt %, 1.5 wt %, and the concentration of NaOH in 0.5wt %, 1.0wt %. Fig. 2.56 is the microscopic picture of microcapsules manufactured under the condition of 0.5wt % chitosan, 0.5 wt % NaOH, and with 0.5-wt % natural coconut oil as amphoteric surfactant. Under this manufacturing condition, good formation and dispersion of microcapsules can be obtained. Wen-Chuan H, Chih-Pong C, Ying-Lin G, in 2006 September [118], discovered that when the chitosan concentration is lower than 0.2 wt%, there is a lot of citronella oil floating on top layer of emulsion. Obviously in the formation process of the microcapsules, the wall membrane of the microcapsules is too thin to completely cover the citronella oil. On the contrary, when chitosan concentration is higher than 0.5wt %, there is no sign of citronella oil on the surface of the emulsion. NaOH plays the role of hardening agent in this experiment. Applying too little NaOH cannot effectively separate out the chitosan to achieve good encapsulation, on the other hand applying too much NaOH can actually cause excessively high viscosity of the entire emulsification system and produce microcapsules in a bulky group formation.

The research shows that the chitosan microcapsules have very good dispersion result with this natural coconut oil amphoteric surfactant. Adding 0.5 – 1.0 wt% natural coconut oil amphoteric surfactant and stir slowly using magnetic agitator, then set

aside for 10 days to observe the microcapsules dispersion effect. The probable causes should be that chitosan solution contains -CH_3COO^- and –NH_4^+ structures, the amphoteric surfactant added, which has both positive and negative ion, will react with -CH_3COO- and -NH_4^+ in the same time, therefore achieve good dispersion effect.

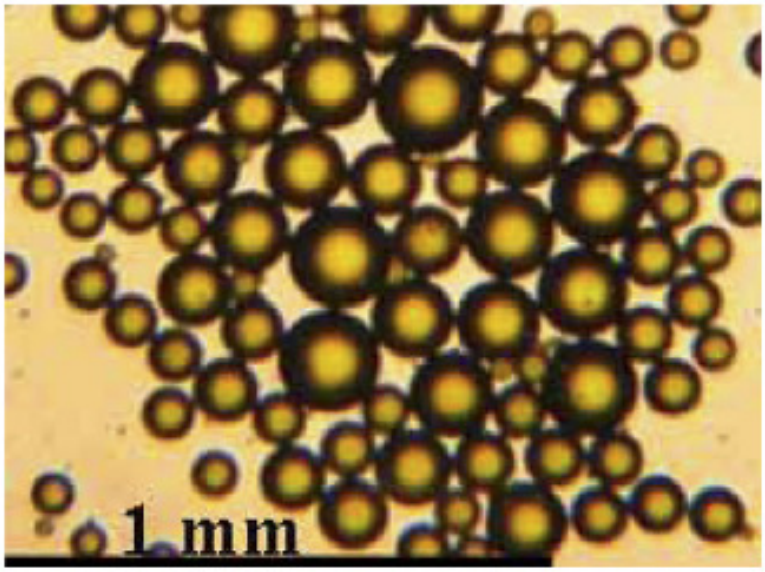


Fig. 2.56: Microphotographs of Chitosan Microcapsules (x80). The Microcapsules were Prepared at The Concentration of 0.5-wt% Chitosan and 1.0 wt% NaOH at 800-rpm Stirring Rate [118]

Release effect of concentration of wall membrane and particle size: Fig. 2.57 shows microcapsules manufactured with chitosan wall membrane in 0.5 wt%, 1.0 wt%, and 1.5 wt% concentrations, and their influences of release effects to the encapsulated volatile citronella oil. The chart demonstrated the sustained release rate of microencapsulated volatile citronella oil is obviously slower than that of not-micro-encapsulated volatile citronella oil; moreover, the thicker the chitosan concentration, the slower the release rate of volatile citronella oil. This is because the thicker the chitosan concentration, the thicker the microcapsules wall membrane and smaller the pore space between chitosan molecules, therefore causes difficulties for the volatile citronella oil release from microcapsules. Thus, Wen-Chuan H, Chih-Pong C, Ying-Lin G, in 2006 September [118], could have better control over the sustained release effect by changing chitosan wall membrane thickness.

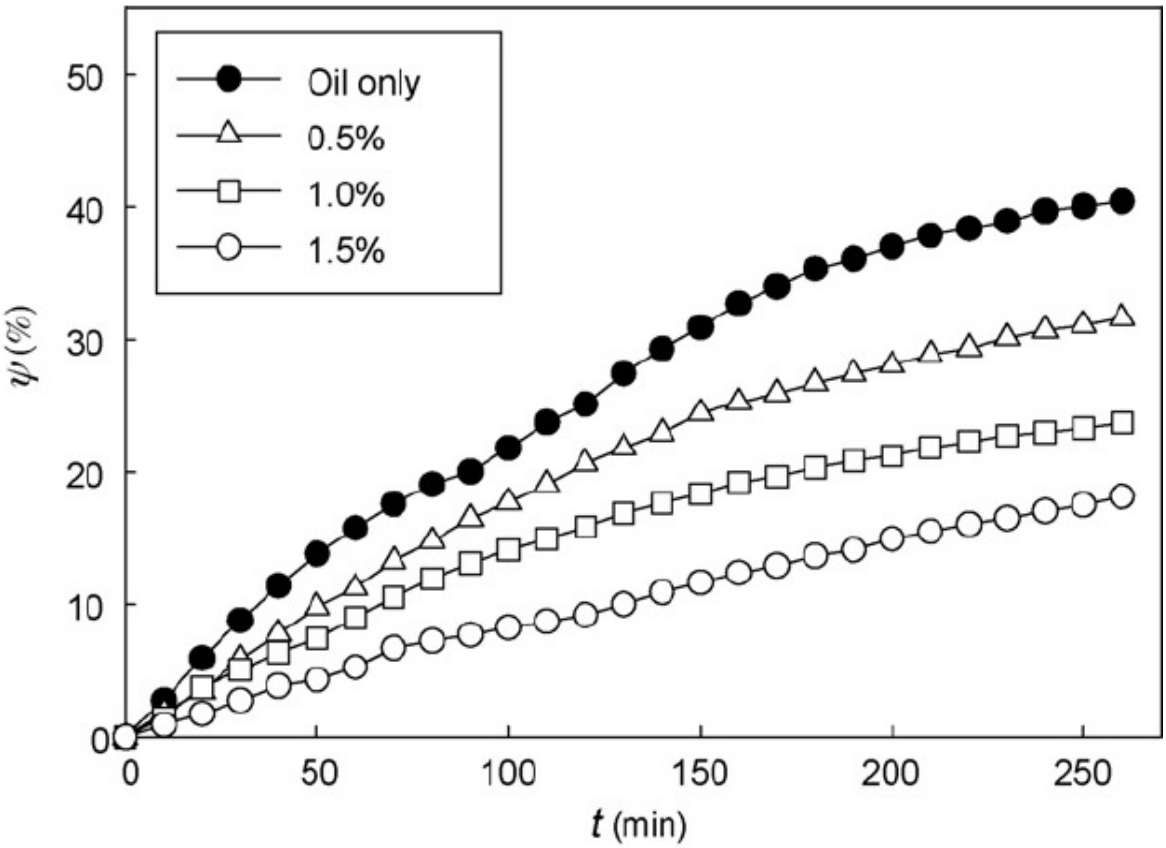


Fig. 2.57: Time Courses of Oil Release From Microcapsules at Different Concentrations of Chitosan. The Samples Prepared at NaOH 1.0 wt%, 800 rpm Stirring Rate. The Symbols (Black Circle), (Triangle), (Square), (White Circle) Denote Concentrations of Chitosan of 0 wt% (Oil Only), 0.5 wt%, 1.0 wt%, and 1.5 wt%, Respectively [118].

In order to observe the influence of the microcapsules particle size to release effect of the volatile citronella oil, Wen-Chuan H, Chih-Pong C, Ying-Lin G, in 2006 September [118], fix the microcapsules manufacturing condition with chitosan concentration in 0.5 wt% and NaOH concentration in 1.0 wt%, and change the emulsion stirring speed at 400 rpm, 800 rpm, and 1.500 rpm. The results are microcapsule samples with average particle sizes of 225±24 μm, 131±20 μm, and 11±3 μm, respectively. Then continue the volatile citronella oil release experiments with these different sizes samples, and study the influences to the release behavior of microcapsules encapsulated volatile citronella oil. The experimental data were plotted in Fig.2.58. From the chart it appears that increase the emulsion stirring speed could produce microcapsules with small particle size, and small particle size can increase the release rate of the volatile citronella oil. This outcome is consistent with the research of the relation between the particle size and sustained release rate by Yamamoto et al. [121]. The reason should be that smaller particle size microcapsules would have larger total specific surface area, therefore causes its release rate to be faster than that of larger particle size microcapsules.

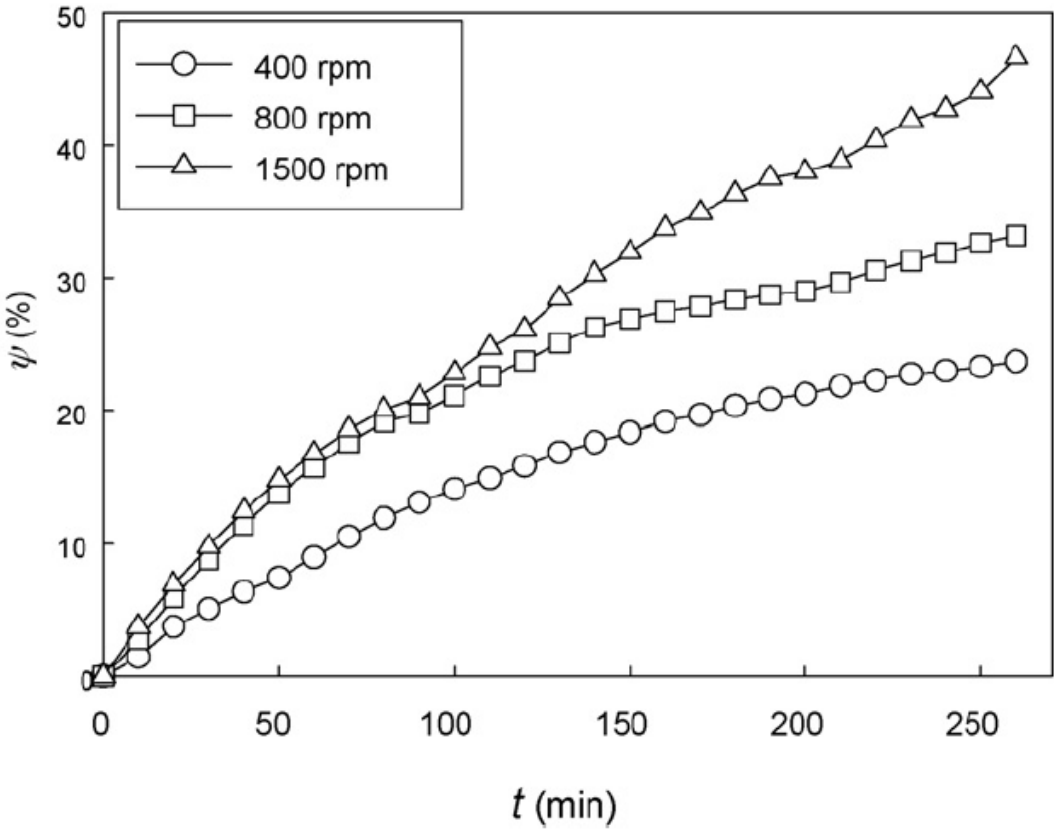


Fig. 2.58: Time Course of Oil Release From Microcapsules at Various Stirring Rate. The Samples Prepared at Chitosan 0.5 wt%, NaOH 1.0 wt%. The Symbols (Triangle), (Square) and (Circle) Denote Stirring Rate 1.500 rpm, 800 rpm, and 400 rpm, Respectively [118]

Also, in the study of M.W. Keller, N.R. Sottos [122], an optimal combination of microcapsule and matrix properties is necessary to ensure mechanical triggering when the material is damaged; if the shell wall is too thick the microcapsule will not rupture readily, preventing the release of healing agent (Nov 2006). On the other hand, if the shell wall is too thin, the capsules not only are fragile, but also allow diffusion of the healing agent into the matrix. Other key parameters for efficient healing agent delivery are the elastic stiffness, the failure strength of the capsules, and the fill content, which is the percentage of the capsule core volume occupied by the encapsulated fluid. Furthermore, capsule failure behavior was found to be highly diameter dependent. Capsules of smaller diameters, while failing at lower loads, have higher normalized failure strength [122].

Release effect of chitosan microcapsules after thermal treatment: The influence of: (1) changes in operation environment temperature and (2) changes in thermal pretreatment temperature and thermal pretreatment time, to the release effects of chitosan microcapsule encapsulated volatile Citronella Oil were investigated. First

the operation environment temperatures is set in 40 °C, 60 °C and 80° C; conduct the sustained release property measurement with microcapsule samples that has not been thermal pretreated, and plotted the results in Fig. 2.59. The manufacturing conditions of the test samples were set at chitosan wall membrane concentration 0.5 wt%, NaOH concentration 1.0 wt%, hardening time 1 h, and emulsification stirring speed 800 rpm. From the graph we could see under the 40 °C and 60 °C operation environment, the oil release rate of encapsulated Citronella Oil of the latter (60 °C) is slightly higher than the former (40 °C) but there is little difference between the two. Yet if the operation environment temperature were increased to 80 °C, the microcapsule encapsulated Citronella Oil has initial low release rate, and declining to nearly none when operation time is close to 50 min. The reason is that the chitosan molecule chains gradually contract because the microcapsule wall membrane was heated and intermolecular space is then reduced; therefore slow down the "Citronella Oil" release rate gradually. So along with the operation time increase, the wall membrane structure highly contracted causing the pores nearly completely seal off and the volatile Citronella Oil unable to continue to release.

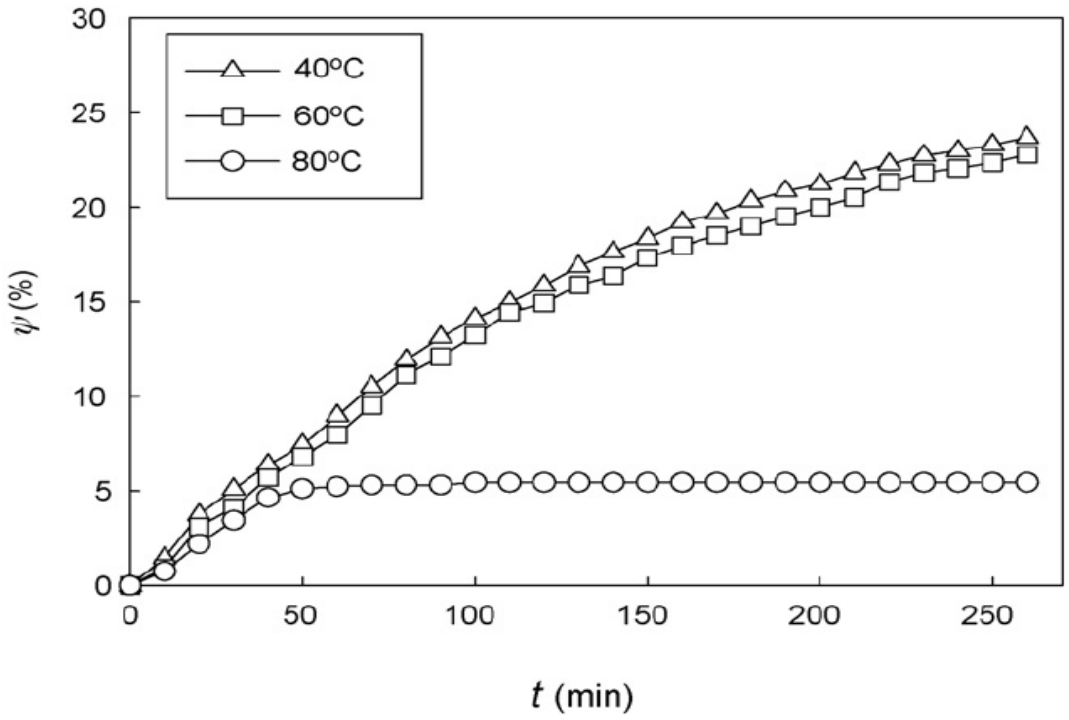


Fig. 2.59: Time Courses of Oil Release From Microcapsules at Various Operation Environment Temperatures. The Samples Prepared at Chitosan 0.5 wt%, NaOH 1.0 wt%. The Symbols (Triangle), (Square) and (Circle) Denote Operation Environment Temperature 40 °C, 60 °C, and 80 °C, Respectively [118]

The results of investigating the release behavior of the encapsulated Citronella Oil after thermal pretreatment in 40 °C, 60 °C and 80 °C for 1 min. are shown in Fig. 2.60 (a). The microcapsules manufacturing conditions are: Chitosan 0.5 wt%, NaOH 1.0 wt%, hardening time 1 h, stirring rate 800 rpm. From the chart we could find the encapsulated Citronella Oil microcapsules release rates after thermal pretreatment in 40 °C and 60 °C have little difference. It is obvious that Chitosan wall membrane structure were not greatly affected when thermal pretreatment in 40 °C and 60 °C for 1 min. But when the thermal pretreatment temperature increased to 80 °C, the release rate of microcapsule encapsulated Citronella Oil rapidly descended. The reason should be as aforementioned that high heat contracted the microcapsule wall membrane structure and close the pores. Fig. 2.60 (b) shows that when other conditions are fixed, with 80 °C thermal pretreatment temperature for 1 min, 5 min, and 10 min, the release states of the encapsulated Citronella Oil. From the graph we could find that the release rate of Citronella Oil slows down when thermal pretreatment time increases. Especially after thermal pretreated at 80 °C for over 5 min, we can find the release rate of the microcapsule encapsulated Citronella Oil approaching zero, the Chitosan wall membrane almost completely seals up. Therefore we could utilize this method of increase the thermal treatment temperature and treatment time to control the sustained release rate of the microcapsules.

If the experiment data were placed into the exponential function Eq. (3) to generate the solid line in the figure, the results are generally consistent with values obtained from the experiment. Thus the oil release curves are fitted well to the exponential function as aforementioned.

It demonstrated that the analysis data are reliable because all the correlation coefficient in the exponential function are greater than 0.97, where C_{eq} means the concentration of oil released at the equilibrium state, τ the time constant and t is the release time. As shown in Fig. 2.61 (a) and (b), increasing the pretreatment temperature and pretreatment time would increase the value of τ. Thus the results indicated that the release rate of volatile Citronella Oil depends on the pretreatment temperature and the pretreatment time considerably.

The results also indicated that the basic effects of formation and dispersion of microcapsules could be attained under the conditions of chitosan concentration is higher than 0.2 wt%, NaOH concentration is higher than 0.5 wt%, and natural

coconut oil was added as the amphoteric surfactant. When the concentration of chitosan wall membrane material is 0.5 wt%, 1.0 wt% and 1.5 wt%, the encapsulation efficiency of microcapsules is 98.2%, 95.8%, and 94.7%, respectively.

The oil release rate increases when the diameter of microcapsules decreases. If the microcapsules have been thermal pretreated in 80 °C temperature, the chitosan wall membrane will shrink and causes difficulties for the “Citronella Oil” to release. This effect is even more noticeable if the time of thermal treatment is longer. Therefore by controlling the concentrations of chitosan and NaOH, the particle sizes of the microcapsules, the pretreatment temperature and pretreatment time, we could control the oil release rate of the volatile Citronella Oil from the chitosan wall membrane. Main results of this study were summarized in Table 2.12.

Table 2.12: Main Results of The Study of Wen-Chuan H, Chih-Pong C, Ying-Lin G

Condition	Result	Reason
Increase on "Chitosan Wall Membrane %"	Increase on release time of Citronella Oil	Because, the thicker the chitosan concentration, the slow rate of volatile citronella oil. The thicker the chitosan, the thicker microcapsule membrane and smaller the pore space between chitosan molecules.
Increase on "Emulsion Stirring Rate"	Decrease the size of microcapsules	This triggered an increase on the release rate of the volatile citronella oil. Because, smaller particle size, microcapsules would have larger total specific surface area; it causes much increase in the release rate than that of larger particle size of microcapsules.
Operation environment temperature increase from 40-60 °C to 80 °C	The microcapsule encapsulated citronella oil has initial low release rate; and in further, declining to nearly none when operation time is close to 50 min.	Because, high heat contracted the microcapsules wall membrane structure and close the pores, and completely seal off and the volatile citronella oil unable to continue to release.
The optimum encapsulation efficiency starts after 0.2 wt % chitosan	When the chitosan concentration is lower than 0.2 wt%, there is a lot of citronella oil floating on top layer of the emulsion.	Because, in the formation process of the microcapsules, the wall membrane of the microcapsules is too thin to completely cover the citronella oil. On the contrary, when the chitosan concentration is higher than 0.5 wt %, there is no sign of citronella oil on the surface of the emulsion.

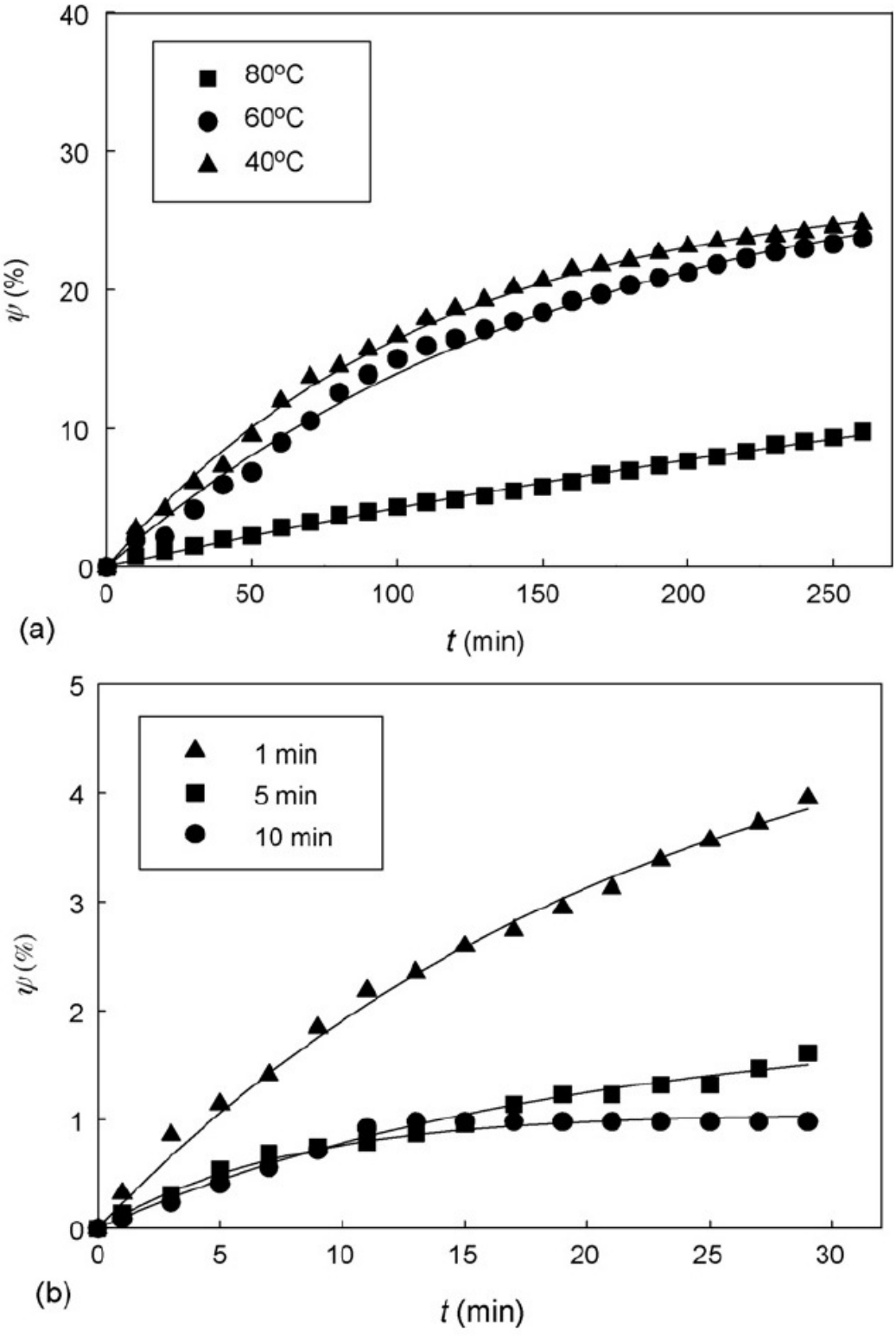


Fig. 2.60: Time Course of Oil Release From Microcapsules at Various Treated Temperatures (a) and Ttreated Times (b). The Samples were Prepared at The Condition of 0.5 wt% Chitosan, 1.0 wt% NaOH. The Solid Lines are Calculated Using Eq. (2.8) [118]

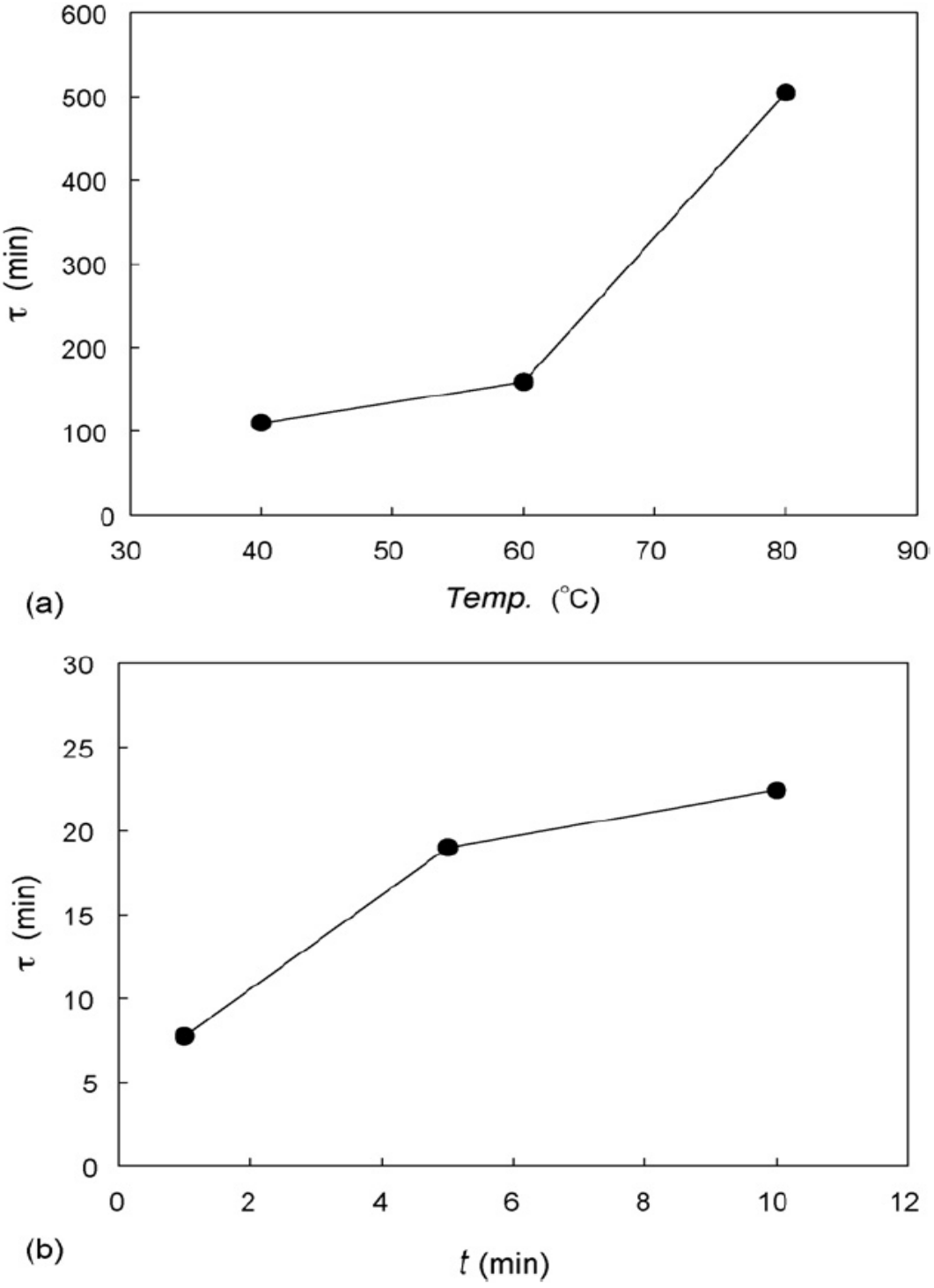


Fig. 2.61: Oil Release From Microcapsules at The Effective Time Constant as a Function of Pretreated Temperature (a) and Pretreated Time (b) [118]

2.7.2. Effect of Chitosan Concentration on Size and Release Behavior

To analyze the effect of chitosan concentration on size and release behavior, Lina Zhang, Yong Jin, Haiqing Liu and Yuming Du made some researches on Bovine Serum Albumin (BSA) [123]. They investigated the swelling behavior, encapsulation efficiency, and release behavior of the microcapsules with different chitosan contents and pH conditions. Their study result indicated that the microcapsules have high encapsulation efficiency (75%) and a suitable size (20-50 μm). The BSA in the microcapsules was speedily released at pH 7.2, namely, in intestinal fluid. The BSA release was reduced with the increase of chitosan content from 17% to 38% in the microcapsules. Acid-treated microcapsules have a compact structure, owing to a strong electrostatic interaction caused by NH2 groups pf chitosan and –COOH groups of carboxymethyl cellulose (CMC), and encapsulated BSA was hardly released at pH 1.0, namely in gastric juice.

Table 2.13: Chitosan Content of The Microcapsules [123]

Microencapsulation		
Chitosan content in 20 ml acetic acid	Microcapsules **with** BSA	Microcapsules **without** BSA
0.2 g	CSCM-B1	CSCM-1
0.4 g	CSCM-B2	CSCM-2
0.6 g	CSCM-B3	CSCM-3

By changing the content of chitosan (0.2, 0.4, 0.6 g) in 20 ml acetic acid, a series of the encapsulation microcapsules were prepared and coded as CSCM-B1, CSCM-B2 and CSCM-B3, and the microcapsules without BSA, coded as CSCM-1, CSCM-2, and CSCM-3. (Table 2.13)

Preparation of Chitosan/ NaCMC Microcapsules: to clarify the compatibility of chitosan in an acidic solution with organic solvent, a 1.67% (w/v) chitosan acid solution was prepared by dissolving 0.25 g of the chitosan in 15 ml of a 2% acidic aqueous solution, in which HCl, acetic acid, ascorbic acid, or citric acid was used as the acid source. An organic solvent such as methanol, absolute ethanol, or acetone was added to each chitosan acidic solution and a precipitation phenomenon was observed. The methanol, ethanol, and acetone possess a hydrophilic property, which is immiscible with hydrophobic liquid paraffin. If the organic solvents were separately added to liquid paraffin, spherical drops of the solvent can be formed by an interfacial phenomenon. However, chitosan does not dissolve in an organic

solvent, but dissolves only in aqueous organic acids. Therefore, the compatibility between the organic solvent and the chitosan acidic solution was determined by eye. Table 2.14 shows the compatibility of four acid solutions of chitosan with three organic solvents. Apparently, the compatibility of methanol and chitosan solution is good, whether in acetic acid, ascorbic acid, or citric acid. Therefore, methanol and acetic acid selected to be used here.

Table 2.14: Compatibility Between Chitosan Acidic Solution and Organic Solvents [123]

Chitosan Solution In	Methanol	Absolute Ethanol	Acetone
Hydrochloric acid	+	++	+++
Acetic acid	-	-	+
Ascorbic acid	-	+	+++
Citric acid	-	++	++
(-) Soluble; (+) insoluble;(++ and +++) larger white precipitate			

Chitosan microcapsules were prepared by the emulation phase-separation method at room temperature. Ten grams of NaCMC powder was previously suspended in 100 mL of liquid paraffin containing 0.7% of span 20. Twenty milliliters of acetic acid with different concentrations of chitosan containing 10 mL of methanol and 1.0 g of BSA were added to the liquid paraffin system to form a water-in-oil (W/O) emulsion, stirring at a speed of 600 rpm for 1h to settle the particles of emulsion. Thereafter, 50 mL ethyl acetate was added in drops to the above system, and the phase separation occurred at the interface of the W/O emulsion to form hard-shelled microcapsules. The microcapsules were suspended in 50 mL ethyl acetate overnight to remove the residual oil and then continued to harden in ethyl acetate. The microcapsules obtained were filtrated, air-dried at room temperature, and then vacuum-dried. The overall process is outlined in Fig.2.62.

SEM photographs of the microcapsules are shown in Fig.2.63. The sizes of the prepared microcapsules are all about 40- 50 μm, and CSCM-1 and CSCM-B1 have a good sphericity. (Fig.2.63 (a) and (b)).

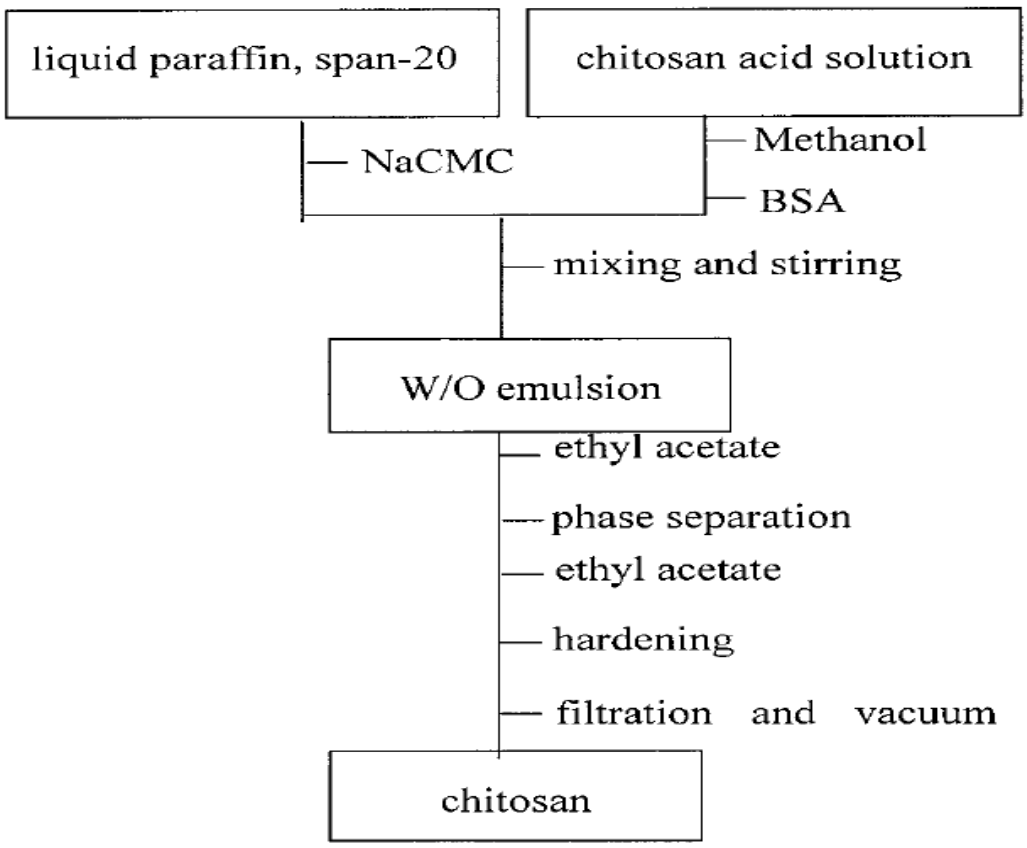


Fig. 2.62: Preparation of Chitosan Microcapsules by Emulsion Separation Method [123]

The surface of the microcapsules was surrounded with some residual CMC. The size of the CSCM-1 microcapsules was smaller than that of CSCM-B1, which encapsulated BSA. Interestingly, the shape of the CSCM- 1b microcapsules was not spherical, and the surface had porous, open channels (Fig. 2.63 d.) This may be caused by weaking of the interaction between CMC and chitosan. However, the acid-treated CSCM-1a microcapsules exhibited a smaller sphere size of 20 μm with a compact structure, which was caused by shrinking after being treated in 0.1M HCl. As shown in CSCM-1a (Fig. 2.63 f), the surface morphology was denser and smoother than was that of CSCM-1, CSCM-B1, and CSCM-1b, suggesting that a strong interaction between chitosan and CMC in the microcapsules occurred in the acidic condition. This is in good agreement with IR results.

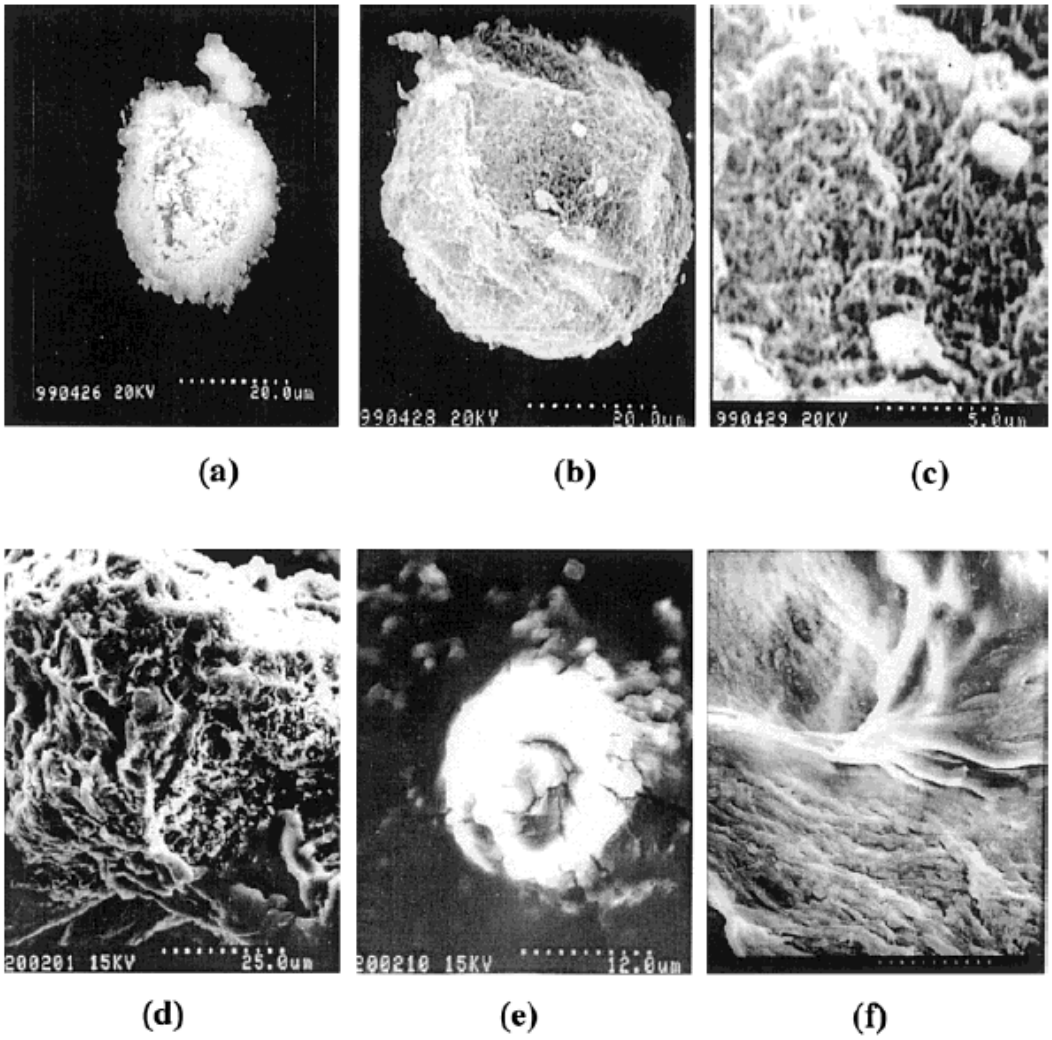


Fig. 2.63: SEM of The (a) CSCM-1, (b, c) CSCM-B1, (d) CSCM-1b, and (e, f) CSCM-1a Microcapsules [123]

Fig. 2.64 shows the X-ray diffraction patterns of CSCM-1 and the microcapsules treated in 0.1M HCl (pH 1.0) and in Tris-HCL buffer (pH 7.2). In view of the X-ray diffraction patterns, the crystallinity of CSCM-1a was higher than that of the others. The relatively low crystallinity of CSCM-1b indicated a decrease in the intermolecular interaction, which caused the release process to quicken. Fig. 2.65 shows the effect of chitosan concentration on the particle size of the microcapsules. Apparently, the particle size decreased with the increase of the chitosan concentration. This can be explained by chitosan and CMC are two oppositely charged polyelectrolytes, and the microcapsule formed an insoluble complex caused by the hydrogen bonding of two polymers.

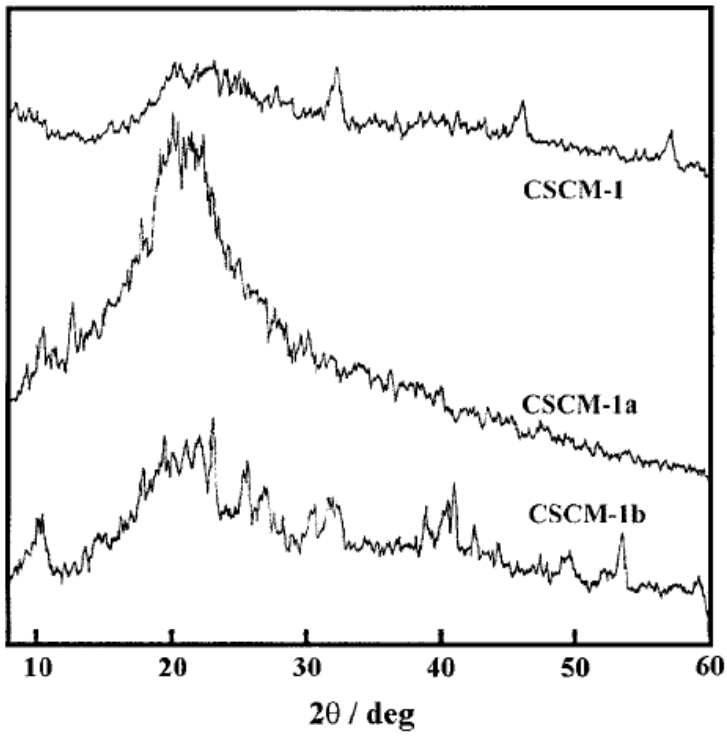


Fig. 2.64: X-ray Diffraction Patterns of CSCM-1a and CSCM-1b Microcapsules Treated with 0.1 M HCl (pH 1.0) and Tris-HCl Buffers (pH 7.2), Respectively, and CSCM-1 [123]

Therefore, the intermolecular interaction of the NaCMC and chitosan increased with the increase of chitosan from 17% to 38% in the capsules, resulting in shrinkage of the particle size. The value of the BSA encapsulation efficiency (AE) of the CSCM-B1, CSCM-B2, and CSCM-B3 microcapsules were calculated to be around 75%, from reproducible results obtained three times. So, the chitosan concentration hardly affected the entrapment of BSA. Compared with the literature, the microcapsules have a relatively high loading capacity. This may be related to the isoelectric point of BSA.

Fig. 2.66 shows the effects of chitosan content on the release behavior of the microcapsules in the Tris-HCL buffer (pH 7.2) at 37°C, which indicated that in the first 5 hour CSCM-B1 released nearly 60% BSA; however, CSCM-B2 and CSCM-B3 only released 35% BSA. After 1 day, CSCM-B1 released 95% BSA, but CSCM-B2 and CSCM-B3 only releases 80 and 65% BSA, respectively. In other words, the BSA in the microcapsules containing more chitosan such as 38% was more slowly released because of a relatively compact surface structure.

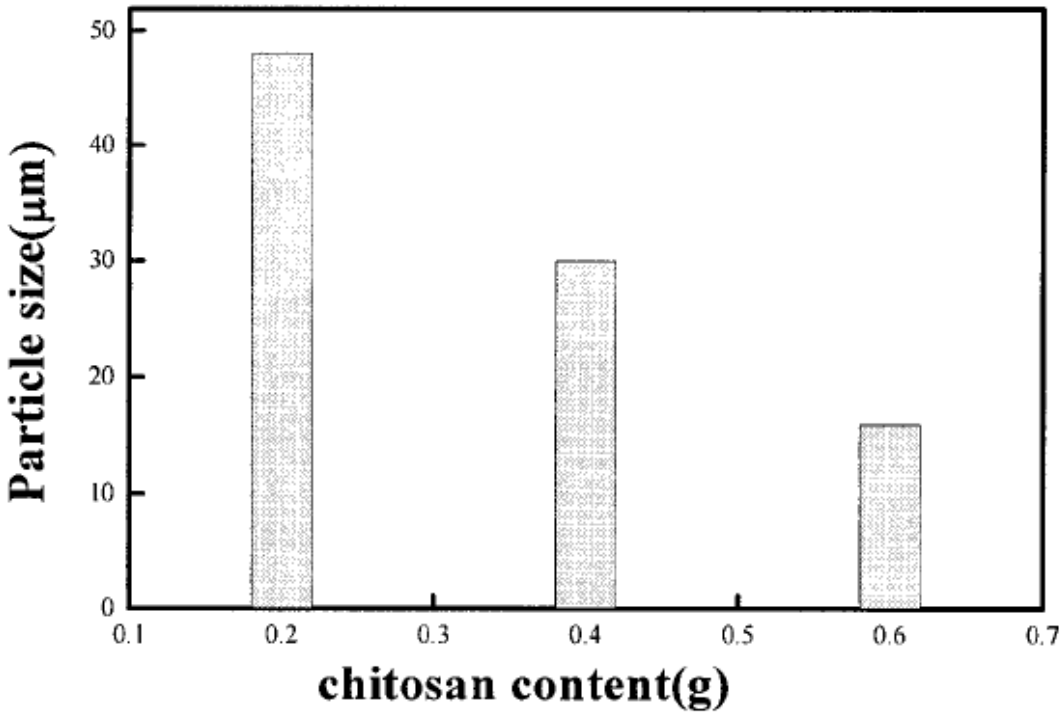


Figure 2.65: Effect of Chitosan on Particle Size [123]

Effect of pH on release: Fig. 2.67 shows the BSA in vitro release behavior of acid-treated and buffer-treated CSCM-1a and CSCM-1b microcapsules. The results indicate that the release of BSA depends obviously on the pH. Compared with the release curve in pH 7.2, a few BSA in the CSCM-1a was released at pH 1.0, owing to the stronger interaction between CMC and chitosan to form a dense surface membrane. In the first 4 hours, only 20% BSA was released from CSCM-1a, while in CSCM-1b; it was more than 50%. The fast release of BSA in pH 7.2 is due to the easy penetration of the buffers into porous microcapsules, quickly inducing the swelling of the polymer. More than 90% of BSA was released from CSCM-1b in 24 hours. Therefore, the microcapsule is pH-sensitive and has potential application in controlled release such as in intestinal fluid or gastric juice.

Effect of pH on swelling of microcapsules: the pH dependence of the swelling of the microcapsules is shown in Fig. 2.68. The microcapsules in 0.1M HCl (pH 1.0) had a lower percentage swelling value, compared to that at pH 7.2. The swelling ability of the microcapsules under an acid environment was weakened. This can be explained in that, in low pH condition, the amino groups from chitosan were protonated and the electrostatic interaction of carboxyl groups of CMC with the

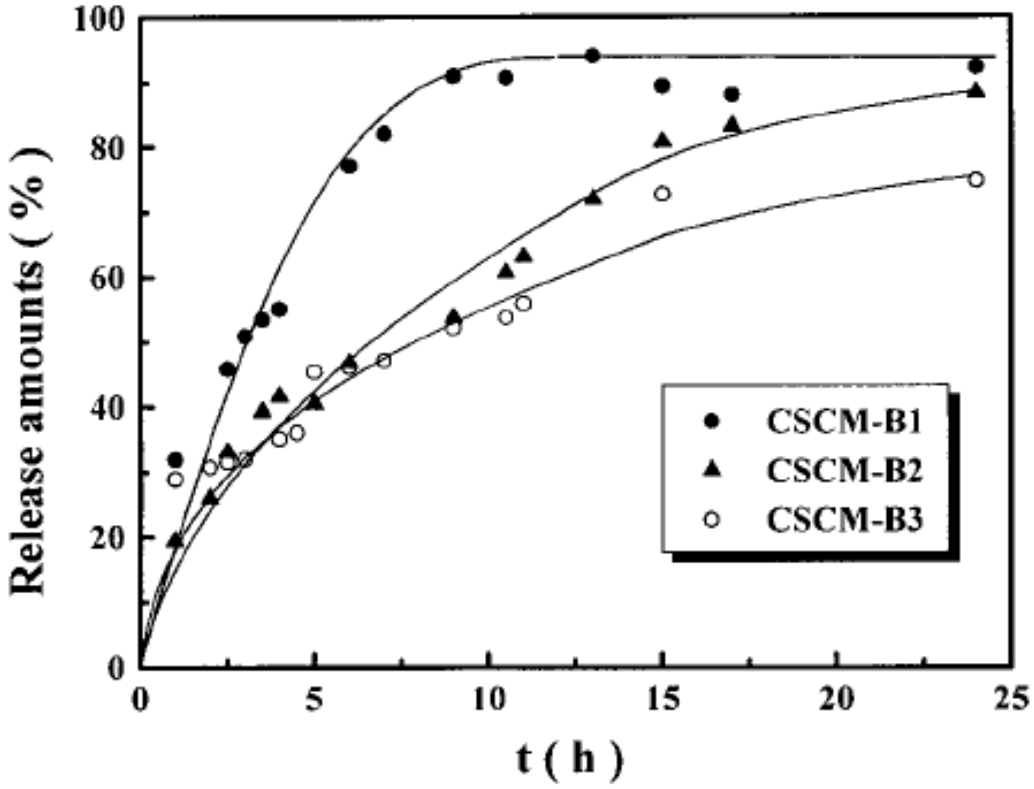


Fig. 2.66: Effect of Chitosan Concentration on BSA Release From The Microcapsules in Tris-HCl Buffer, at pH 7.2 and 37°C [123]

amine groups of chitosan were strengthened, resulting in a dense structure. The conclusion was supported by the SEM result in Fig. 2.63.

In conclusion, the microcapsule spheres encapsulating BSA were preliminary prepared from chitosan and NaCMC using a novel method of emulsion phase separation. The BSA encapsulation efficiency was around 75%. The size of the microcapsules ranged from 20 to 50 μm and changed with the chitosan content and acid treatment. The BSA in the microcapsules was speedily released in the Tris-HCL buffer (pH 7.2), namely, in intestinal fluid, and the release decreased with increase of chitosan content from 17 to 38% in the microcapsules.

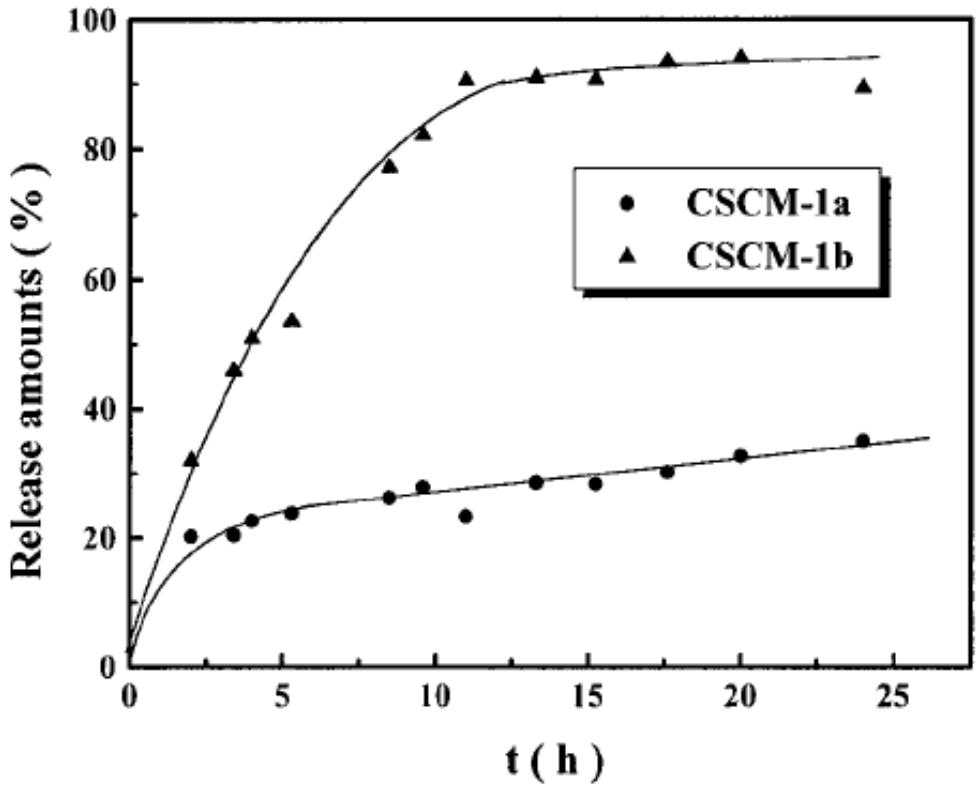


Fig. 2.67: Time (t) Dependencies of BSA Release From Microcapsules Being Treated in 0.1M HCl (pH 1.0) and Tris-HCl Buffers (pH 7.2) [123]

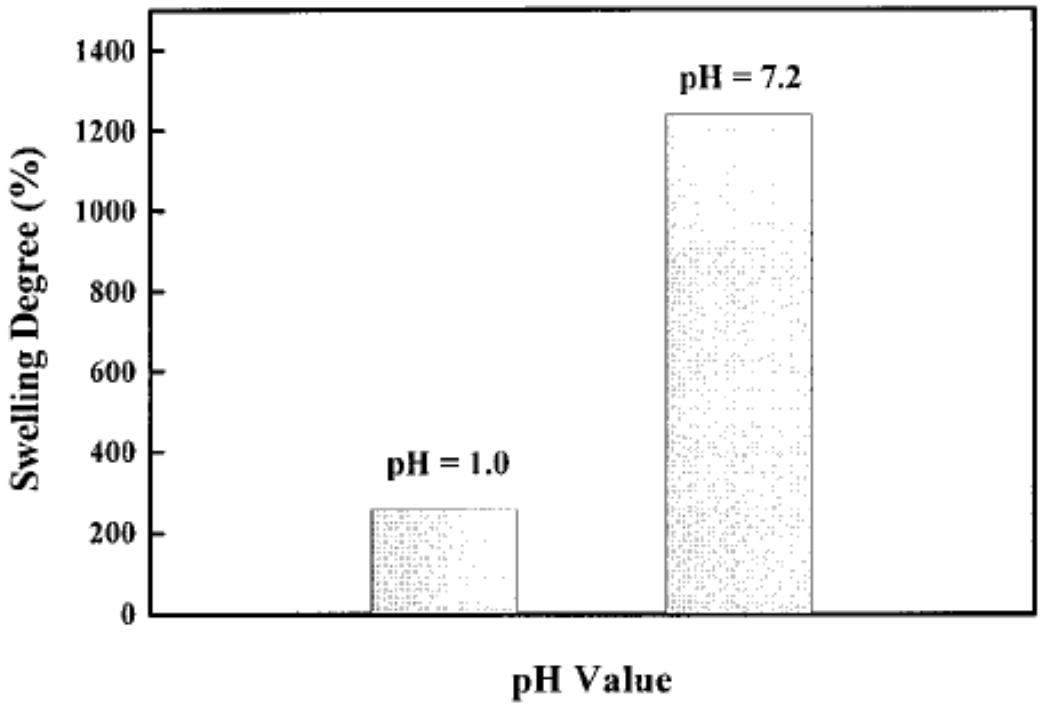


Fig. 2. 68: Swelling Degree of The Microcapsules in Different pH Conditions [123]

The dry microcapsules were immersed in 0.1 M HCl (pH 1.0) at room temperature for 24 hours to obtain acid-treated capsules, which have a compact structure, owing to a strong electrostatic interaction caused by –COOH groups of CMC and $–NH_2$ groups of chitosan. The encapsulated BSA in the acid-treated microcapsules was hardly released at pH 1.0, namely, in gastric juice. The main summary of this study is given in Table 2.15.

Table 2.15: Main Results of of The Study of Lina Zhang, Yong Jin, Haiqing Liu and Yuming Du

Condition	Release Time	Reason
pH decrease	The release time of BSA microcapsules gets longer	Acidic conditions owe the stronger interaction between CMC and chitosan to form dense surface membrane. In acidic condition, microcapsules gets swollen less than alcalic ones. In low pH condition, the amino groups of chitosan were protonated and the electrostatic interaction of carboxly groups of CMC with the amino groups of chitosan was strengthened, resulting a dense structure
Chitosan concentration increase	The release time of BSA microcapsules get longer	More chitosan means, relatively more compact surface structure; more surface structure causes the strengthening of the capsule resistance.
Chitosan concentration increase	The release time of BSA microcapsules get longer	Because, the particle size decreased with the increase of the chitosan concentration. This can be explained by chitosan and CMC are two oppositely charged polyelectrolytes, and the microcapsule formed and insoluble complex caused by the hydrogen bonding of two polymers. Therefore, the intermolecular interaction of the NaCMC and chitosan increased with the increase of chitosan from 17% to 38% in the capsules, this results in shrinkage of the particle size, so, more compact structure of microcapsule means more durable properties.

2.7.3. Release Properties of Insulin From Polysaccharide Microcapsules

In the study of Shiqu Ye, et al. [124]; weakly cross-linked melamine formaldehyde micro-particles with diameter of 2.1 μm were prepared as sacrificial templates. Alginate and chitosan multi-layer microcapsules were fabricated by the layer-by-layer self-assembly on the MF micro-particles followed by removal of the template through dissolving at low pH. Insulin was spontaneously loaded into the ALG/CHI microcapsules when it was positively charged owing to the existence of negatively charged complex of ALG/MF residues inside the capsules. The insulin loading capacity increased when the solution pH values decreased from 4.0 to 1.0. When the two-temperature loading process was applied, loading insulin at two temperatures of 20 and 60 °C (one hour for each) not only increased the loading capacity but also slowed down the insulin release rate due to more compact multi-layer shell formed at higher temperature. The release rate of insulin in pH 7.4 buffers was much faster than that in pH 1.4 buffers due to the charge reverse of insulin induced by the pH

change. Cross-linking ALG in the capsule shell with calcium ions (Ca^{2+}) or coating the insulin-loaded microcapsules with additional layers remarkably decreased the insulin release rate. These results provide novel methods to control the loading and release properties of protein with these polysaccharide microcapsules.

2.7.3.1 Controlled Release From Microcapsule

The insulin release from the ALG/CHI microcapsules was investigated at pH 1.4 and 7.4. Fig. 2.69 shows the cumulative insulin release curves at these two pH values. The insulin is released very slowly at pH 1.4 and only 14.2% of the loaded insulin can be released after 6 h. While at pH 7.4, a much fast release is observed. About 50% insulin has been released within the first 80 min, and then the release rate decreases and the curve gradually levels off as the cumulative release amount reaches ~80%. This significant difference of insulin release with the change in solution pH is also resulted from the insulin ionization. The loaded insulin is positively charged at pH 1.4 as mentioned above, thus strongly attracted with the negative ALG/MF complex inside the microcapsules, restricting the release. The insulin charge becomes negative at pH 7.4 and preferentially moves into the solution from the microcapsules due to the electrostatic repulsion, leading to a rapid release.

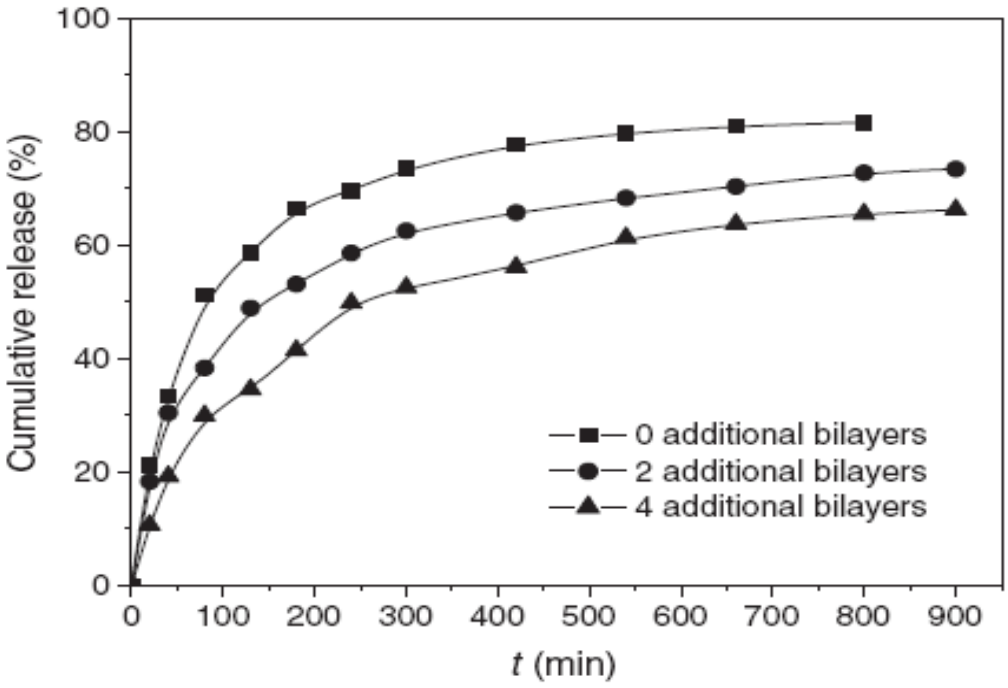


Fig. 2.69: Insulin Release From (ALG/CHI)5 Microcapsules at Indicated pH [124]

The release curves at pH 7.4 for insulin from the (ALG/CHI)5 microcapsules loaded with the two-temperature loading at different second temperatures are depicted in Fig.2.70 the release rate becomes slower as the second loading temperature is higher. When the second loading temperature is 60 °C, the release rate is the slowest and the curve levels off at the cumulative release amount of ~44%. As mentioned above, higher loading temperature produces a more compact shell wall for the ALG/CHI microcapsules, which blocks the insulin molecules from penetrating to the bulk solution. The present release behavior can be consistently explained with the temperature effect on the loading capacity. Thus, the loading temperature provides a simple way not only to increase the insulin loading capacity but also to control the release rate of drug loaded in the microcapsules.

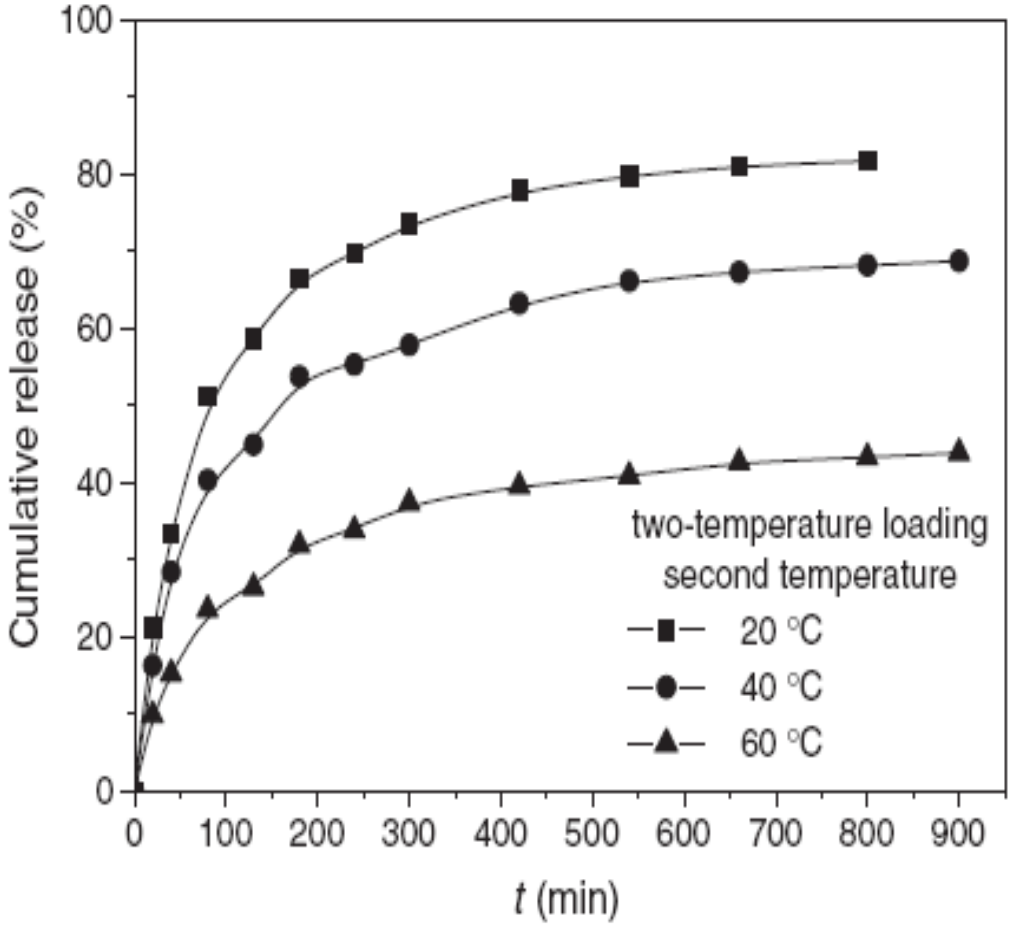


Fig. 2.70: Release Profiles of Insulin From $(ALG/CHI)_5$ Microcapsules Loaded with Two-temperature Loading at Indicated Second Loading Temperature [124]

Shiqu Ye, et al, March 2006 [124]; found that the release rate of acridine hydrochloride became slightly slower when the ALG in the ALG/CHI multi-layer shell was cross-linked with glutaraldehyde [125] Here, we investigate the insulin release from the same ALG/CHI microcapsules with the ALG cross-linked after loading. The diazoresin/PSS microcapsule shell cross-linked with UV irradiation has been found to lead to a decrease in the multi-layer film permeability [126-128]. But this method requires the synthesis of diazoresin and the multi-layer film assembled in dark. Hence, the calcium ion (Ca^{2+}) was chosen as the cross-linker in this work for the ALG in the multi-layer film. The release profiles in Fig. 2.71 indicate the reduction in the release rate and cumulative release amount due to the cross-linking of ALG with Ca^{2+} in the ALG/CHI multi-layer shell. Because the cross-linking restricts the ALG chain moving in the shell and enhances the obstruction to the insulin movement passing through the microcapsule shell.

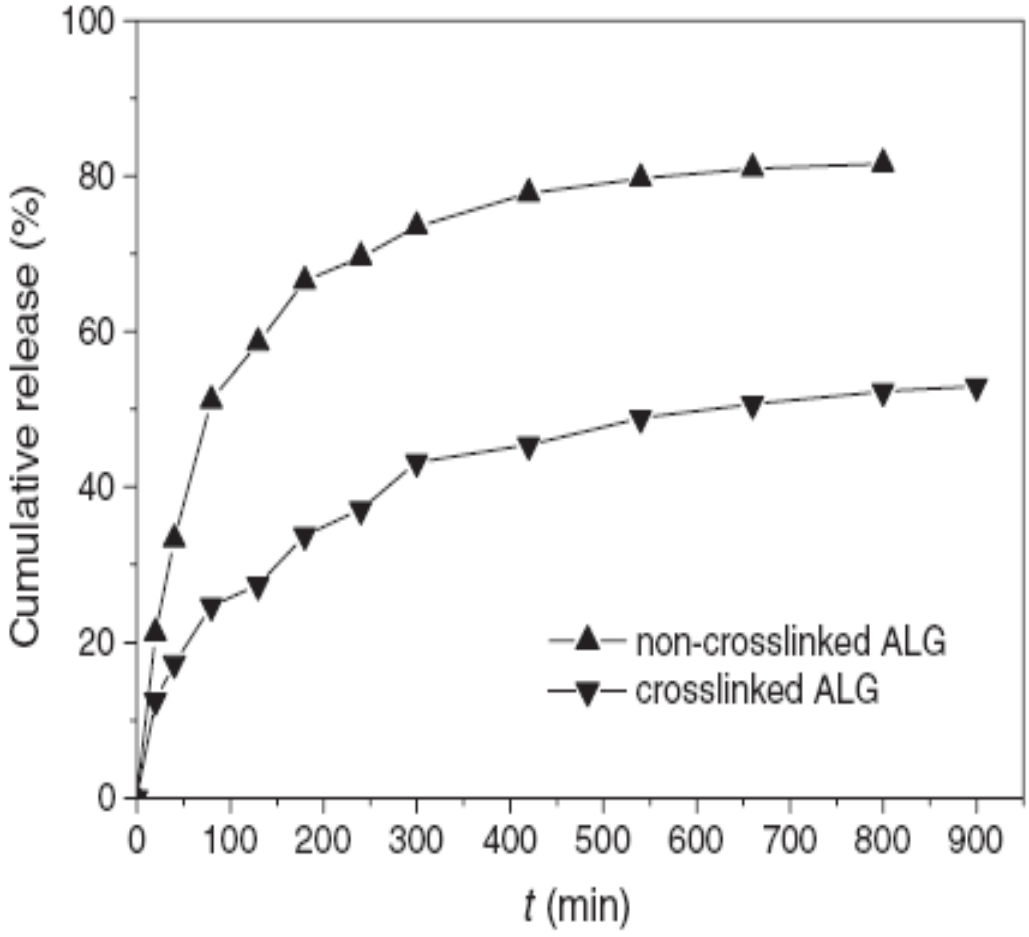


Fig. 2.71: Release Profiles of Insulin From $(ALG/CHI)_5$ Microcapsules Before and After Cross-Linking ALG with Ca^{2+} Ions [124]

The loaded microcapsules can be coated with additional polyelectrolyte layers to reduce the release rate further [129]. In Shiqu Ye, Chaoyang Wang, Xinxing Liu, Zhen Tong, Beye Ren and Fang Zeng experiment, this process caused 34~46 wt.% loss of the insulin already loaded in the microcapsules, which is much smaller than 70 wt.% loss reported by Balabushevich et al. for coating the dextran sulfate/protamine microcapsules with additional layers [130]. The insulin release from the ALG/CHI microcapsules with additional deposited polysaccharide layers is obviously slowed dawn compared with that without additional deposited layers as shown in Fig. 2.72. The additional deposited layers on the loaded microcapsules will give rise to an extra barrier to the insulin molecule movement, thus slow down the release rate.

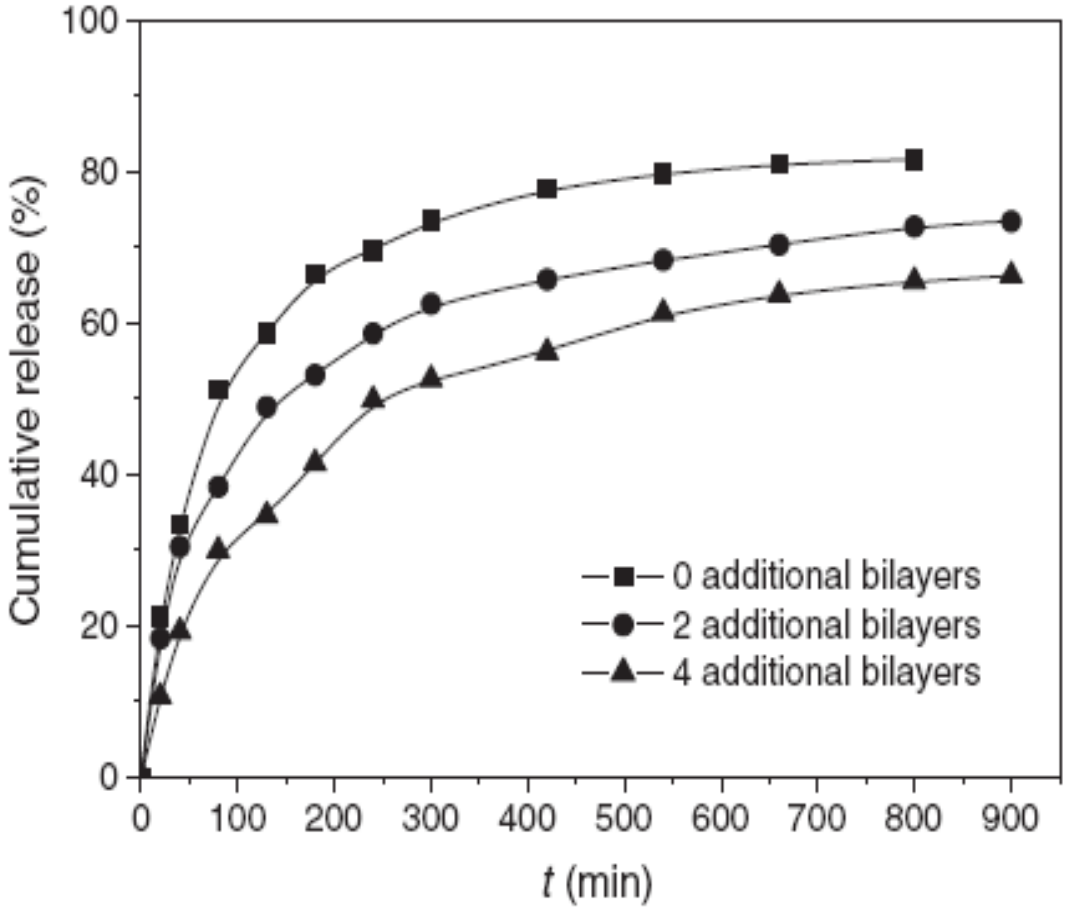


Fig. 2.72: Release Profiles of Insulin From (ALG/CHI)5 Microcapsules Coated with Additional Layers After Loading [124]

The main summary of this study was listed in Table 2.16.

Table 2.16: Main Results of The Study of Shiqu Ye, Chaoyang Wang, Xinxing Liu, Zhen Tong, Beye Ren and Fang Zeng

Condition	Result	Reason
pH 1.4 and pH 7.4 condition comparison	pH 7.4, the release rate of insulin in pH 7.4 was much faster than that of pH 1.4. In pH 1.4, only 14.2% of the loaded insulin could be released after 6h. While 50% of inslulin in pH 7.4 is released	Due to charge reverse of insulin by pH change. This significant difference of insulin release with the change in solution pH is also resulted from the insulin ionization. The loaded insulin is positively charged at pH 1.4, therefore strongly attracted with the negative ALG/MF complex inside the microcapsules, restricting the release. The insulin charge becomes negative at pH 7.4 and preferentially moves into the solution from microcapsules due to the electrostatic repulsion, leading to a rapid release.
Second loading temperature increase	Release of insulin gets slower	Higher loading temperature produces more compact shell wall for the ALG/CHI microcapsules, which blocks the insulin molecules from penetrating to the bulk solution.
Comparison of crosslinked and non-crosslinked ALG	Crosslinked ALG results in the reduction in the release rate and cumulative release amount due to the cross-linking of ALG with Ca2+ in the ALG/CHI multilayer shell	Because the cross-linking restricts the ALG chain moving in the shell and enhances the obstruction to the insulin movement passing through the microcapsule shell.
Increase on the number of the membrane layers	Slow down the insulin release speed	The additional deposited layers on the loaded microcapsules will give rise to an extra barrier to the insulin molecule movement, thus slow down the release rate

2.8. PCM (Phase Change Material) Microcapsules

A series of heat energy storage microcapsules was prepared using melamine-formaldehyde resin as the shell material and the mechanical properties of the shell were investigated in the study of Juenfeng Su, Li R, Lixin W[131]. A phase change material whose melting point was 24°C was used as core and the quantity of heat involved in phase transition was 225.5 J/g. Average diameters of the microcapsules varied from 5 to 10 μm, and the globular surface was smooth and compact. The mechanical properties of the shell were evaluated by observing the surface morphological structure change after application of pressure by means of scanning electron microscopy. When the mass ratio of the core and shell material is 3:1, a yield point of about 1.1×10^5 Pa was found and when the compression was increased beyond this point the microcapsules showed plastic behavior. This has been attributed the cross-link density and to the high degree of reaction of the shell material. Different yield points subsequently reflected differences in the mechanical behavior. It was also found that the mechanical intensity of double-shell microcapsules was better than that of single shelled ones.

Microencapsulation of PCMs (microPCMs) provides a means to solve the super-cool problem and interfacial combine with circumstance materials. MicroPCMs have been used in functional fibers [132,133], solar energy utilization [134], heat energy transfers [135], agriculture [136], and building materials [137]. However, they require considerable intensity in practical use and it is not easy to get accurate results. Sun and Zhang [138,139] had investigated the strength of microcapsules made of three different shells using a micromanipulation technique. A single microcapsule was compressed to obtain a large deformation or rupture and the force applied was measured simultaneously. This method required the use of a special apparatus, as it was difficult to see the surface shape straightaway. Also when microPCMs were used in practice, the strength of a single microcapsule could not reflect the actual strength as the microcapsules were all piled together.

Thus, there is a need for a simplified method to evaluate the mechanical properties of microPCMs. The objective of the study of Juenfeng Su, Li R, Lixin W, [131] was to synthesize microcapsules containing composite PCMs of size 5 μm for application in controlling indoor wall temperatures, which would save energy and make indoors comfortable. MicroPCMs were prepared using in- situ polymerization with pre-polymer of melamine-formaldehyde and their rigidity was characterized. Microcapsules were placed between two pieces of glass and were compressed. (Fig. 2.75) The rigidity of the shell was evaluated by observing the surface morphological structure change by means of scanning electron microscopy after application of pressure.

The pre-polymer of melamine-formaldehyde was obtained from Shangai JQ Chemistry Co., China, and its solid content was 50%. The composite PCMs, whose main constituent was lauryl alcohol (prepared by Energy Sources and Low emission Research Institute of Hebei University University of Technology)., was applied as core material. The phase change temperature was 24 °C and the quantity of heat involved in phase change was 225.5 J/g. Styrene maleic anhydride copolymer solid (Scripte-520) was used as a dispersant. Nonionic surfactant, NP-10 (poly (ethylene glycol) nonyphenyl) obtained from Sigma Chemical, was used as an emulsifier.

The encapsulation was carried out in a 500 ml three-neck round-bottom flask equipped with a condensator and a tetrafluorethylene mechanical stirrer. First, 10g of

styrene-maleic anhydride and 0.8 of NaOH were dissolved in 100 ml water at 50 °C, the pH value being 4-5 after 2 h. To the aqueous surfactant solution 32 g of the core was added and the mixture was emulsified mechanically ar a stirring rate of 2.500 rpm for 10 min using QSL high-speed disperse machine. The emulsition was immersed in the bottle dipping in steady temperature flume and stirred at the rate of 1.500 rpm while 16 g of pre-polymer was being immersed at a rate of 0.5 ml/min. The shell was produced after 1.5 h by increasing the temperature to 60°C slowly. Then 16 g pf the pre-polymer in the bottle was immersed at the same rate. The temperature was then increased to 75 °C and after 1 h it was decreased to the atmospheric temperature. The resultant microcapsules were filtered and washed with water and dried in a vacuum oven.

Characterizations: microcapsules were placed between two pieces of glass, 4 cm X 2 cm, and compressed. The intensity measured by a pressure sensor under the bottom glass and data were directly obtained. The rigidity of the shell was evaluated by observing the surface morphological structure after application of pressure by means of a XL30 PHILIPS scanning electron microscope.

Shape of the microcapsules: after the microcapsules were dried in a vacuum oven at 40 °C for 24 h, their morphologies could be observed from the SEM photographs in Fig.2.73. Most of the microcapsules have a smooth surface and the shape is often rounded with an average diameter of about 5 μm. There is no coagulation between particles and the diameter of the microcapsules has a considerable size distribution. As the core material could not be encapsulated completely and the shell material also could not absolutely be covered on the cores, Fig. 2.73 shows minimal polymer piling between microcapsules.

The rate of immersion of the shell material could control the morphology of microcapsules. Microcapsules, both magnified 20.000 times by SEM in Fig. 2.74 a and b, were obtained by an immersion rate of 1 and 0.5 ml/min. With the increase in the immersion rate of the shell material, the surface was rougher. The reason is probably due to the pre-polymer of melamine-formaldehyde will not capsulated on core slowly and tightly at rapid dropping speed.

Shell strength of the microcapsules: microcapsules containing PCM required certain intensity in practical use. Juenfeng S, Li R., Lixin Wang, [157], were adapted a new

method to obtain the intensity. As Fig. 2.75 shows, microcapsules were placed between two pieces of glass and were compressed. The rigidity of the shell is evaluated by observing the surface change after pressure application by means of scanning electron microscopy. The average diameter of the microcapsules was found to be 5 μm and the globular surface was smooth and compact.

The microcapsules whose mass ratio of core and shell material was 3:1, after compression as Fig. 2.76 (a) shows, demonstrated concaves on microcapsules. When the microcapsules were compressed to before a certain point, there was no change on the surface. However, when the deformation was beyond a "yield point", there was profound hysteresis and the microcapsules showed a plastic behavior.

A yield point of about $1.1X10^5$ Pa was found and when the compression exceeded this microcapsules showed plastic behavior. As the compression increased, some small microcapsules caved-in on large ones as are seen in Fig. 2.76 (b). However, no rupture was occurred.

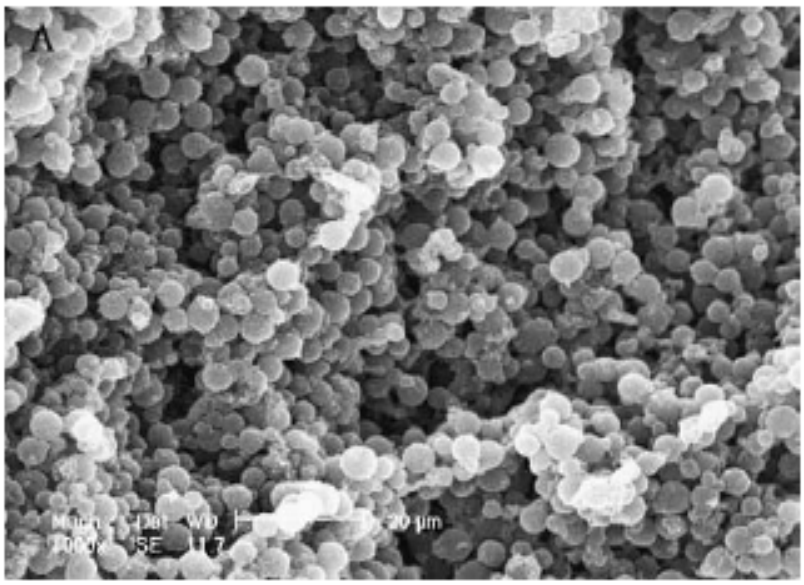


Fig.2.73: SEM Photograph (X1000) of Microcapsule Morphology, Which Dried in a Vacuum Oven at 40 °C for 24 h [131]

From SEM micrographs, of the surface of microcapsules following compression, a yield point, just as the deformation needed mixture force, could be observed. It was also found that the mechanical intensity of double-shell microcapsules was better than that of single shells.

Obviously, there was an influence of core material on the yield point, but this was not considered in this study. The microcapsules were representative of the core-shell structure. Thus from the global strength formulae it is known that the main factors affecting the strength of the shell are thickness and tightness.

Therefore, the yield point expected to be induced by the relationship of the core and shell. If the emulsification speed of the core material is uniform, then the core has the same average diameter; so the thickness is determined by the mass ratio of the core and shell. Tightness reflects the reaction temperature and velocity. These two factors, which were a result of piled cross-link molecules, can be regulated in the preparation process by controlling the parameters. In order to know the effects of yield point on mechanical properties, three tests have been carried out at room temperature in a universal mechanical testing device. These tests evaluate the effects of the immersion rates of shell material, different mass ratio of core and shell material and single-shell and double shell.

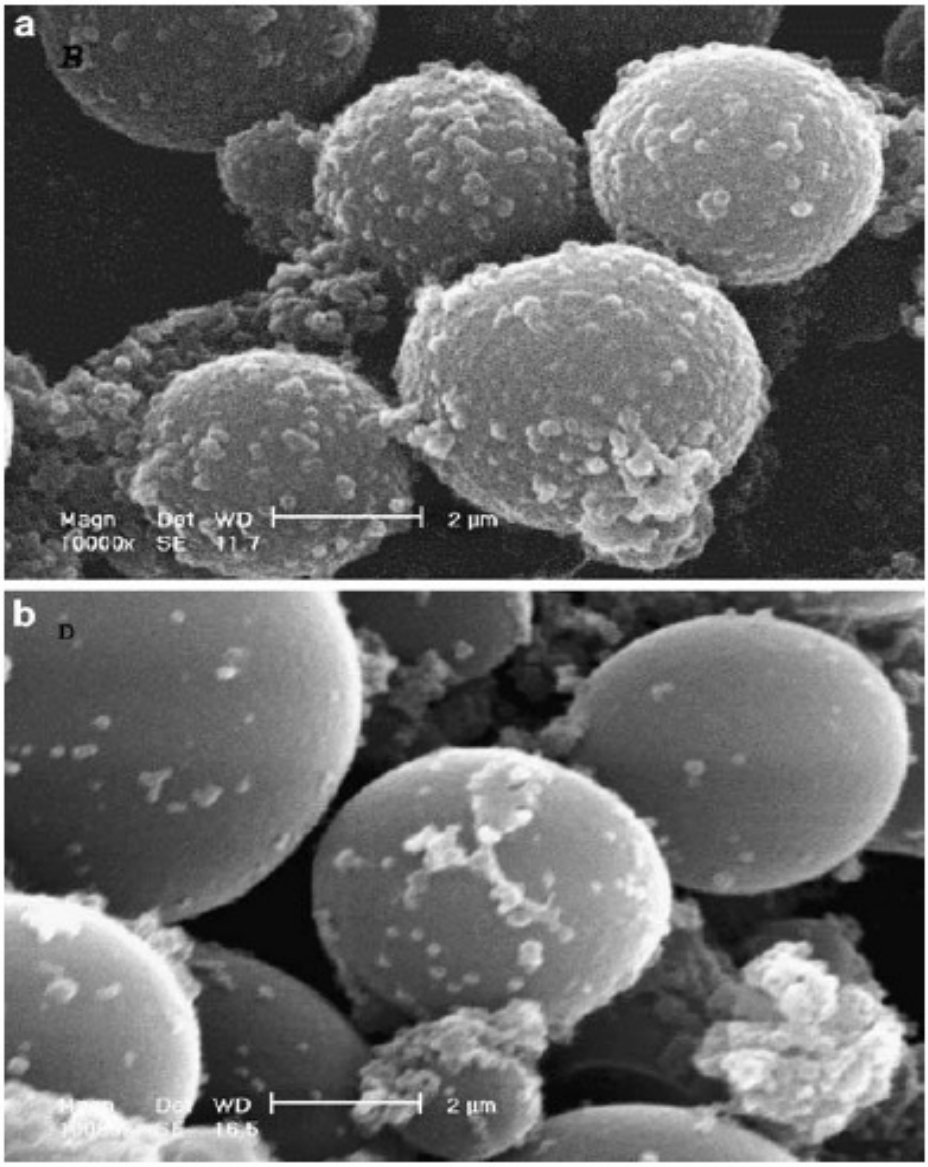


Fig. 2.74: SEM Photographs (X10.000) of Microcapsules Obtained by Shell Material Immersion Speed of a) 1 ml/min and b) 0.5 ml/min. With The Increase of Immersion Rate, The Surface was Rougher [131]

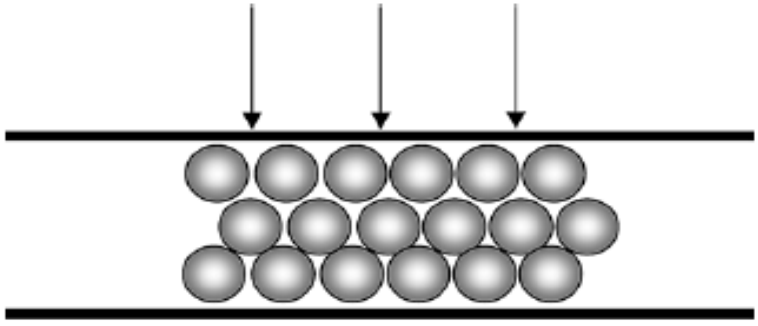


Fig 2.75: Sketch Map of Microcapsules Placed Between Two Pieces of Glass and Compressed. The Rigidity of The Shell is Evaluated by Observing The Surface Change After Pressure Application by Means of Scanning Electron Microscopy [131]

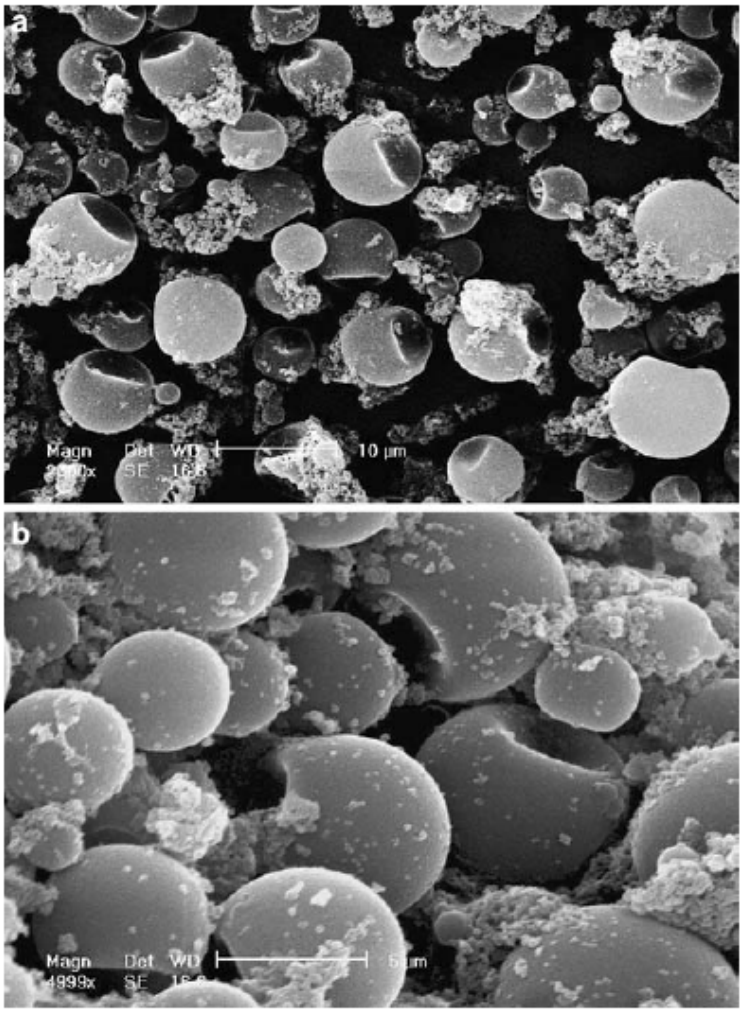


Fig 2.76: SEM Photographs of Microcapsules Whose Mass Ratio of Core and Shell Materials was 3:1 After Compression. As a) x2.000 Shows, There were Concaves on Microcapsules. As Compression Increased, Some Small Microcapsules Caved-in on Large Ones b) x4.999 [131]

Fig. 2.77 shows the variation of yield point of the shell for different immersion rates of the shell material, 0.5, 1.0 and 2.0 ml/min, during encapsulation process. The values decrease as the mass ratio of core and shell increases. The reason is that the shell is not closely knit and there are lacunas or capillaries in the shell at high immersion rates. At lower rates of immersion, the smooth, orbicular shell increases the strength. Preceding microencapsulation, the core material was dispersed by mechanical stirring. The diameter of the dispersed core determined the average diameter of the PCMs. Thus, the same stirring speed, same immersion rate and different thickness of the shell and a different penetration property. The different mass ratios of core and shell microPCMs intensities are shown in Fig 2.77. A mass ratio of 1:1 was slow that of 3:1 and 4:1.

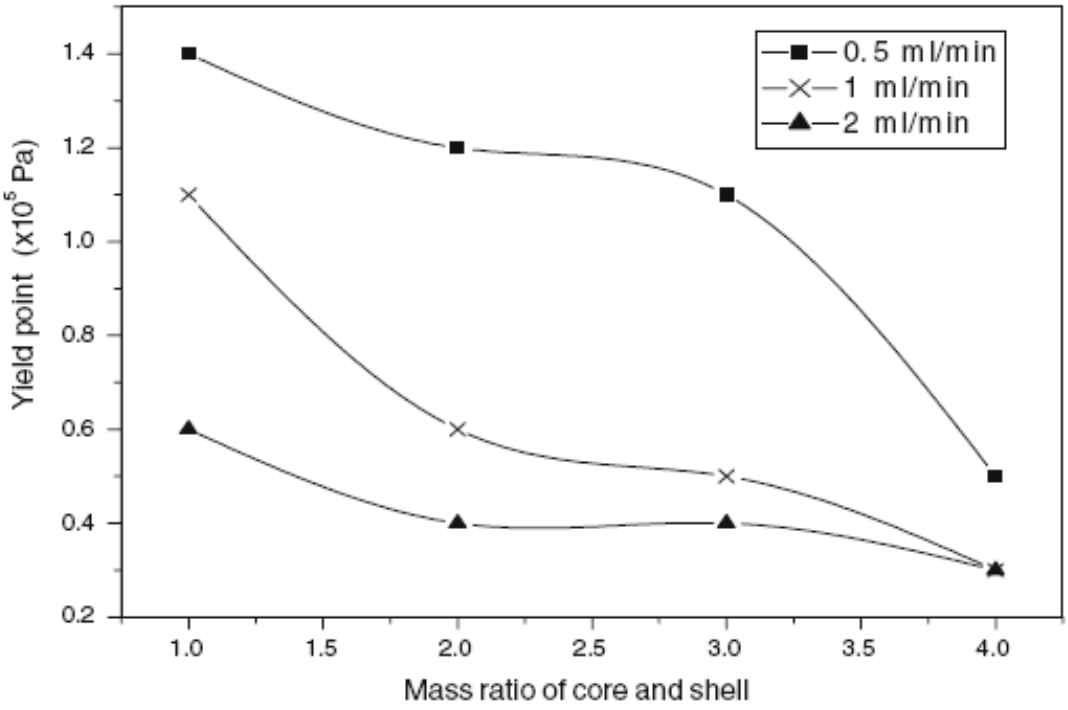


Fig. 2.77: Variation of The Yield Point of The Shell for Different Shell Material Immersion Rates, 0.5, 1.0, and 2.0 ml/min, During The Encapsulation Process [131]

The microcapsule used in the study of Juenfeng Su, Li Ren, Lixin Wang was composed of double melamine-formaldehyde resin shell, which was produced by the slow immersion of the shell polymer material twice [131]. On contrast, a single-shell microencapsulation with different mass ratios of core and shell materials by immersing the shell material continuously at the same speed, 0.5 ml/min, and obtained the yield point as shown in Fig. 2.78. It was also observed that the strength of the shell decreased rapidly. However, when the mass ratio of core and shell is close to 4, there is little difference between the two. MicroPCMs were produced to absorb, store and release large amounts of latent heat, and thus it is expected to encapsulate as much more core material to get a better effect. At the same time, the shell strength has to be taken into account in practical use. Thus it is crucial to balance both sides. After all experimental studies, a mass ratio of 3:1 was found to yield the best results.

From the SEM photographs it can easily be observed the transformation and can be evaluated the structure of the shell. The optimal encapsulation process can be used to obtain a high yield point of the shell. The crucial point, though, is to form an intact core-shell structure. Double shell will make the intact easier.

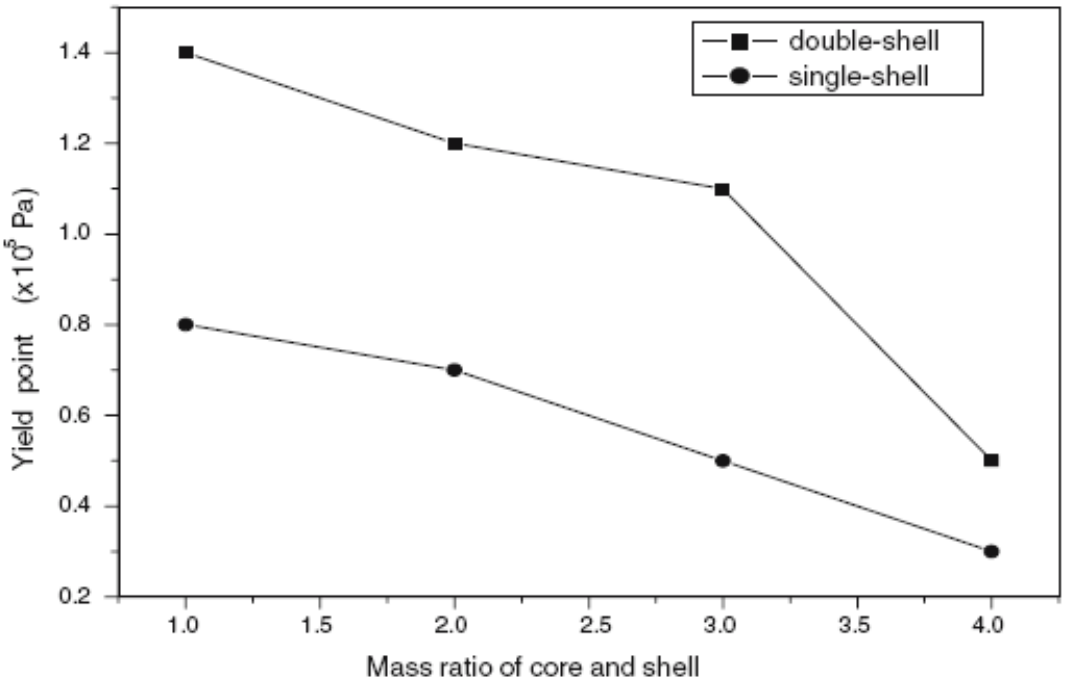


Fig. 2.78: Single-shell and Double-shell Microencapsulation with Different Mass Ratio of Core and Shell Materials Obtained by Immersing The Shell Material Continuously at The Same Speed 0.5 ml/min and Thus Obtaining The Yield Points [131]

Jun-Feng Su, Li-Xin Wang, Li Ren together with Zhen Huang [140] made some further researches in the area of phase change material (PCM) and they studied on the mechanical properties and thermal stability of "double-shell" thermal-energy-storage microcapsules.

Double-shell-structured microcapsules encapsulating phase-change materials (micro-PCMs) with an average diameter of 5-10 μm were successfully fabricated with a melamine-formaldehyde resin as the coating material. The mechanical properties of the obtained piled micro-PCMs, tested under compression, and were evaluated with a pressure sensor. Typical stress-strain curves showed that both the single-shell- and double-shell-structured microcapsules had yield points and maximum point pressures. The morphological changes in the shell surface confirmed the existence of yield points by scanning electron microscopy. When the pressure was beyond the yield point, the microcapsules showed conventional plastic behavior, and the double-shell structure was more mechanically stable than the single-shell one. Differential scanning calorimetry analysis results revealed that the properties of the phase-change materials experienced no variation after coating with a single-shell- or double-shell-structured polymer. Thermo-gravimetric analysis showed that the double-shell-structured micro-PCMs experienced a weight loss of only about 5% from 86.3 to

232°C but did so more rapidly from 232 to 416°C. Thermoregulation was determined with periodical heating and cooling tests. The data showed that the micro-PCMs changed temperature in a narrow range of 20-25°C with a time lag of 20 min to reach the maximum or minimum temperature in comparison with a reference temperature of 18-28°C.

Recently, the ever-increasing energy consumption problem has attracted many researchers around the world, and some energy-saving innovations and technologies thus have been made. Among them, phase-change materials (PCMs) have received much attention because they can absorb, store, and release large amounts of latent heat over a defined temperature range when experiencing a phase transition. PCMs thus can be potentially used for thermal energy storage in many fields. In all these applications of PCMs, microcapsules encapsulating phase-change materials (micro-PCMs) offer an alternative measure for dealing with the super-cooling problem and interfacial combination with environmental materials. This idea can be traced back to the 1990s, and now a number of studies have shown that micro-PCMs are promising for practical use in functional fibers, solar energy utilization, heat-energy transfers, and building materials.

In this work, micro-PCMs were prepared through an in situ polymerization of a melamine-formaldehyde (MF) pre-polymer on the chosen PCM. To make the formed coating compact and thermally stable with excellent process durability, Jun-Feng Su, Li-Xin Wang, Li Ren together with Zhen Huang established a two-step polymerization technique to form micro-PCMs with a double-shell structure. The main feature for preparing the double-shell microcapsules was the addition of the MF pre-polymer in two steps to control the polymerization behavior.

Nowadays, formaldehyde residue has emerged as a health concern for living beings and is the main reason for many indoor air-pollution cases. For this reason, the MF pre-polymer used in this work had a rather low free formaldehyde concentration. Moreover, urea and ammonium persulfate were introduced into the polymerization system to react with dissociated formaldehyde, leading to the thorough removal of formaldehyde from the final products. Besides, the micro-PCMs were tested and thus proved to be harmless to health, and they had no negative effect on interior air quality according to Chinese standards.

In conclusion, a serious of micro-PCMs were prepared to absorb, store, and release large amounts of latent heat for application in energy fields. Thus, Jun-Feng Su, Li-Xin Wang, Li Ren together with Zhen Huang expected to encapsulate the core material as much as possible for a better effect. The shell strength had to be taken into account for prolonging the service time. The mechanical properties of single-shell-structured micro-PCMs and double shell ones were dynamically investigated with a home- made compression design. Jun-Feng Su, Li-Xin Wang, Li Ren, and Zhen Huang' experimental results showed that double-shell-structured micro-PCMs performed very well and seemed to provide a solution to the aforementioned concern. SEM analysis was successfully used to identify the typical process of the shell deformation. All the micro-PCMs were observed to have a yield point and a burst point, but the double shell ones had higher values than the single-shell ones, indicating that the double-shell-structured micro-PCMs were more mechanically stable. The core material encapsulated in the double shell was found to not change its characteristic phase-transition temperature, and this is promising for practical applications.

Phase Change Materials on Polyester Fabrics: In the study of Kyeyoun C and Gilsoo C, [141], melamine formaldehyde (MF) microcapsules containing octadecane are synthesized by the interfacial polymerization method, and the size, the shape, and thermal storage / release properties of the synthesized microcapsules are analyzed by FTIR, SEM and DSC. Polyester fabrics are then coated with the microcapsules under various conditions of concentration and time/ temperature by the knife-over-roll (KOR) and screen printing (SP) methods. The thermal, mechanical and physical properties of the untreated and treated fabrics are evaluated to identify the adhesive method. The mean diameter of the microcapsules ranges from 1 to 1.5 μm, and their shapes are almost spherical. Under the optimum treatment concentration, temperature and time, thermal properties after five launderings decrease rapidly, and the bending and shear rigidities of the KOR fabrics are higher than those of the SP fabrics. This means that fabrics coated by SP become less stiff and hard than those by KOR. SP fabrics exhibit higher air permeability and lower hygroscopic properties than KOR fabrics.

Clothing is comfortable when humans feel physical, physiological, and mental satisfaction as heat and moisture transfer efficiently from the body to the

environment through the clothing [142]. Therefore, development of intelligent fabrics, including thermal storage/release ones, which can adjust and maintain comfort as circumstances change, is very important and necessary.

The design and development of a functional textile providing an ability of dynamic heat regulation next to the skin have attracted more and more attention in recent years. Number of attempts in this field is extensive parallel to the researches in electronics, several solar energy-based systems, buildings, etc. However, successful applications are limited and still under investigation. A remarkable group of them concerns with the manufacture of microcapsules so that spherical bi-component particles consist of shells and surrounded core material [143-150].

Phase change materials (PCMs) have been applied to the textiles in a variety of processes to improve thermal comfort of end-use products, due to their high heat storage capacities. Coating, lamination, finishing, melt spinning, bi-component synthetic fiber extrusion, injection molding, foam manufacturing are some of the convenient processes for PCMs' incorporation into the surface. Well-known PCMs are linear chain hydrocarbons known as paraffin waxes (or n-alkanes), hydrated slats, polyethylene glycols (PEGs), fatty acids and mixture or eutectics of organic and non-organic compounds. PCMs have also been used as a core material in the microcapsule production, the prior stage of aforementioned processes for the fabrication of thermo-regulated fibers, fabrics, coatings and foams [151-153].

Research on adapting microcapsules containing phase change materials (PCM) is currently under way, and the preferred PCMs for textiles are n-paraffin waxes with the various melting and crystallization points according to their carbon numbers [154,155]. Octadecane is particularly suitable for clothing because its melting point is about 28.2 °C. Such a PCM absorbs a large amount of heat and releases that heat in a slush state, which is below the mean skin temperature of 33.3 °C [156-158]. Microencapsulation makes the microcapsules containing PCMs durable and safe through the finishing processes [159]. Fabrics treated with microcapsules containing PCMs must maintain their thermal properties in the bulky state and must absorb, store, and release heat and endure friction and repeated launderings. When PCMs are added to textiles, they release heat as liquid changes to a solid state and absorb heat as the solid returns to a liquid state [160].

In the study of synthesizing polyurea microcapsules (Kyeyoun C and Gilsoo C, [141] containing octadecane [161], microcapsules under 1 μm were compounded by interfacial polymerization, the microcapsules were broken, and the core material was released during the coating process due to low stability to solvent. In the research and development of thermostatic fabrics using the thermal storage/ release properties of polyurea microcapsules containing octadecane [162], the best finishing conditions for the thermal properties were 60 °C/ 8 minutes, which is very low, to satisfy the general curing temperature of 100-140 °C. Therefore, development of more dyrable microcapsules through choice of pertinent shell materials is needed. Melamine-formaldehyde (MF) is an outstanding shell material due to its highly embossed three-dimensional structure and superior to thermal stability [163], and compared to polyurea, M/F is easy to synthesize by the interfacial polymerization method.

There are various coating processes such as knife-over-roll, knife-over-air, pad-dry-cure, gravure, dip coating, and transfer/ cast coating [164]. Of these methods, the knife over roll (KOR) has been used to coat fabrics [165]. But fabric handle worsens with this method, so an improved adhesive method is needed. So, Kyeyoun C and Gilsoo C, 2004, have adopted the screen- printing (SP) method as an alternative for improved coating.

The objective of Kyeyoun C and Gilsoo C's in 2004 is to present the fundamental data for developing thermal comfort clothing. For this, they synthesized the MF microcapsules to compare their thermal storage/release properties with the KOR and SP coating processes, and investigate the effects on launderability, mechanical and hygroscopic properties, and air permeability by examination before and after treatment.

Experimental: Microcapsules were synthesized by interfacial polymerization using melamine and formalin (M/F, Aldrich) as monomers in an emulsion system based on previous research [166]. Octadecane (Aldrich, 99%), was used as the core material and styrene maleic anhydride was the emulsifier. The size and the shape of the synthesized microcapsule containing octadecane were confirmed by FTIR and SEM.

A 100% polyester fabric was chosen as the specimen. Yarn type and weave type and weave were filament and plain, thickness was 0.28 mm, and weight was 42 g/m^2

(Korea Apparel Testing & Research Institute). The coating mixture was made by mixing microcapsules with an acrylic binder (Koplex TF-125) and urethane (Waung Chang R 01 binder) at a ratio of 9:1 in accordance with preliminary tests. Coating mixture concentrations were 2:8 (20%), 3:7 (30%), and 4:6 (40%), the ratio of microcapsule to binder. The surface of the KOR fabrics was coated fully but the SP surface was coated partially according to the screen shapes of the dots (Fig. 2.79) under the same pressure and with the same amount of coating mixture. But the thickness and weight if the SP and KOR fabrics were different due to the holes in the screen printer, even though the coating mixture were controlled. The treated fabrics were placed in a baking apparatus (Daiei Kagaku Seiki Mfg. Co., Ltd.) under fixed temperatures and times of 100 °C/ 2 min and 110, 120, and 140 °C/ 1 min, which were the conditions of perfect dryness at a concentration level of 30%.

Thermal storage/ release properties of microcapsules and specimens treated with microcapsules containing octadecane were analyzed by differential scanning calorimeter (DSC). The storage property was determined by measuring the melting temperature (T_m) and heat of fusion (H_f) at 10-50 °C, and the release property by measuring crystallization temperatures (T_c) and heat of crystallization (H_c) at 50-10 °C. The heating and cooling rates of the DSC run were both 10 °C/min. Heat of fusion and heat of crystallization were obtained by calculating the peak area of the DSC curve.

To test launderability, the specimens were washed in a Kenmore automatic washing machine with AATCC standard detergent 124 in a normal washing cycle and tumble dried according to AATCC 135-1992. The concentration of microcapsules was 30%, and heat temperature/ time for treated fabrics was 110 °C/ 1min. Thermal properties were then measured after one, five, and ten launderings. Microcapsules attached to the fabrics before and after laundering were observed by SEM.

Mechanical properties, including tensile, bending, shear, compression, surface, thickness and weight measured by the KES-FB system [167], air permeability by the automatic air-permeability tester (KES-F8-AP1, Kato Tech Co., Ltd., Japan) and hygroscopic properties by the oven balance method (ASTM D2402-01).

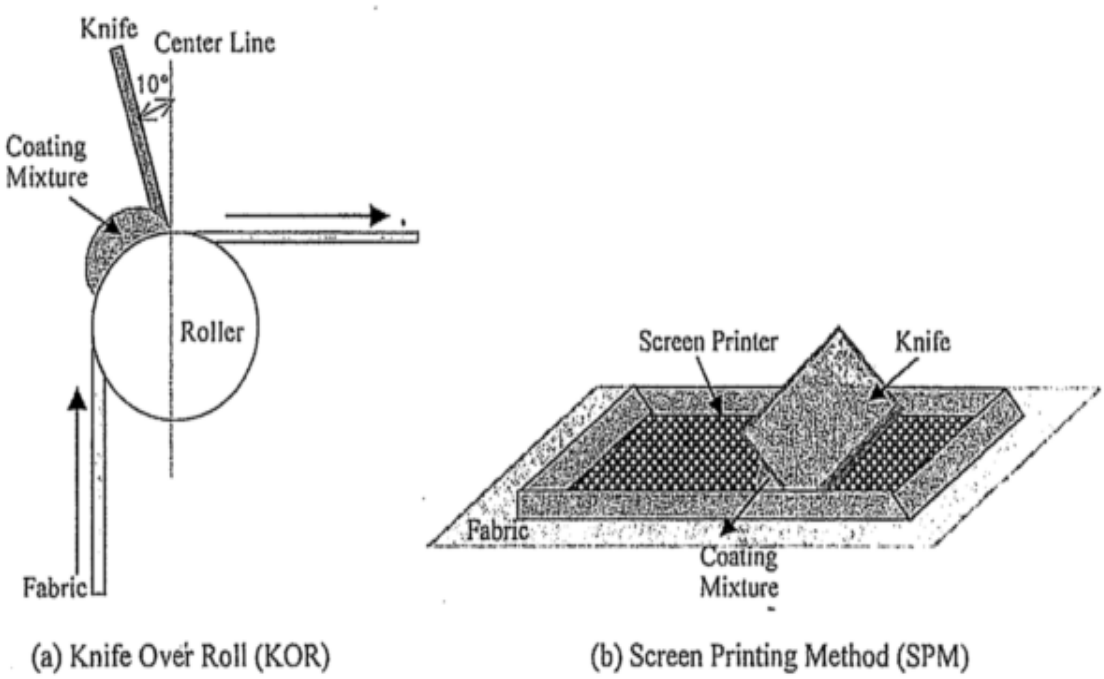


Fig. 2.79: Diagrams of Adhesive Methods [141]

Confirmation of microcapsules: Fig. 2.80 presents the FTIR graph, the microcapsules containing PCMs showing specified peaks of octadecane, the C-H stretching peaks. From this result, it already confirms the successful synthesis of microcapsules.

According to the SEM picture (10.000X), the microcapsules were almost spherical in shape and the size was about 1-1.5 μm. Fig. 2.81 shows the DSC curves of MF microcapsules containing octadecane. Tm was in the range of 28-30 °C and ΔH_f was 140.55 J/g when octadecane melted. T_c was in the range of 20-25 °C and ΔH_c was 133.16 J/g when octadecane crystallized.

Thermal storage/ release properties of treated fabrics: In order to investigate the optimum treatment conditions for microcapsule coated fabrics, Kyeyoun C and Gilsoo C's in [141] examined the thermal storage/ release properties of the fabrics under various treatment concentrations and curing time/temperature combinations with SP. The treatment condition with higher heat content was considered optimum

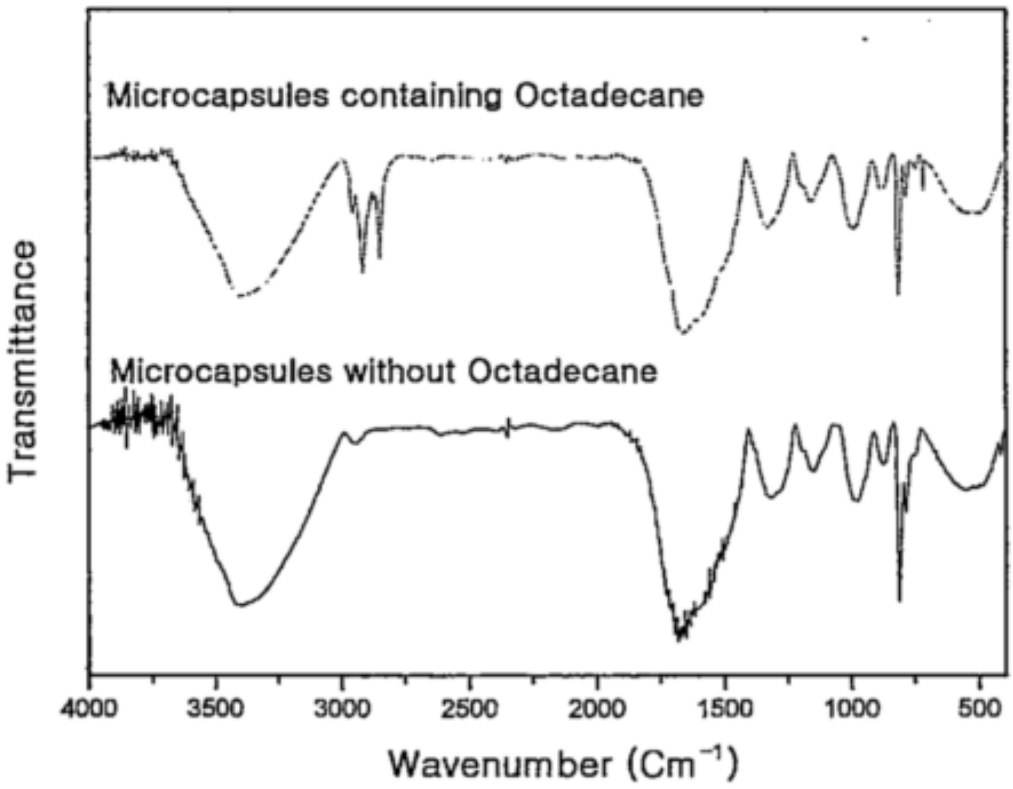


Figure 2.80: FTIR of M/F Microcapsules [141]

Table 2.17 shows the DSC results of ΔH_f and ΔH_c fabrics treated according to concentrations of the microcapsules. Heat contents were 3.478 – 7.651 J/g for ΔH_f and 2.837 – 7.235 J/g for ΔH_c, and the maximum heat content value was observed at 30% concentration. The amount of microcapsules attached to the fabric at 40% concentration became smaller than that at 30% because the coating mixture became too thick to handle. The optimum concentration of coating mixture to the fabrics was therefore determined to be 30%.

Table 2.17: Thermal Properties of Treated Fabrics According to Concentration at 110 °C/ 1min by SP Method [141]

Concentration, %	T_m, °C	DH_f, J/g	T_c, °C	DH_c, J/g
20	28.000	3.478	22.100	2.837
30	27.733	7.651	20.633	7.509
40	29.421	7.368	21.012	7.235

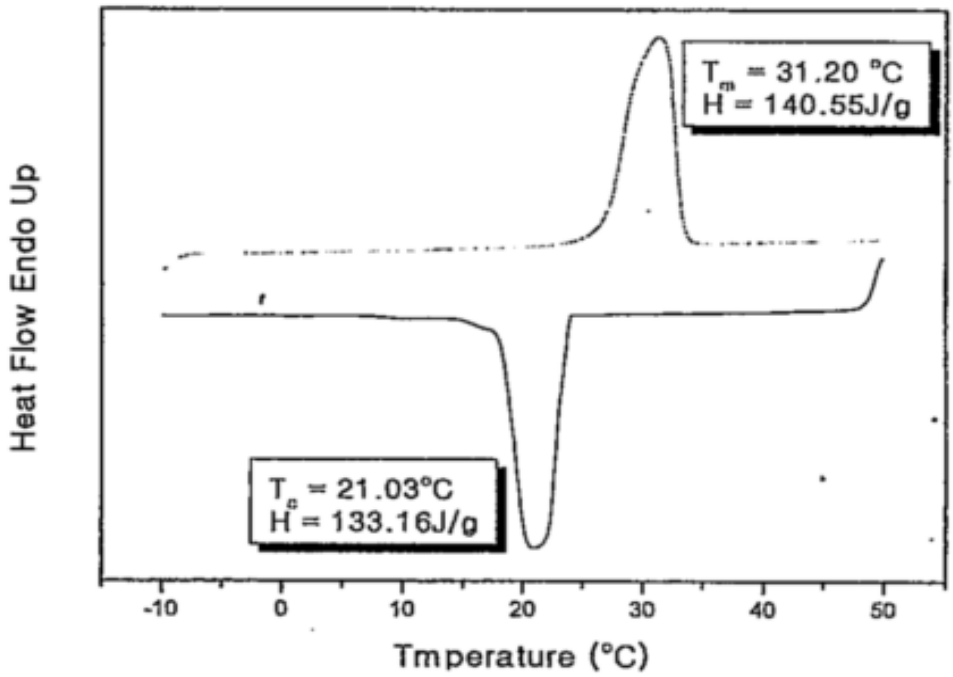


Fig 2.81: DSC Diagram of MF Microcapsules Containing Octadecane [141]

Table 2.18 shows the DSC results of fabrics treated according to the curing temperature/ time. ΔH_f and ΔH_c were 0.794- 7.651 J/g and 0.334 – 7.509 J/g, respectively, and the maximum value of the curing temperature and time was 110 °C/ 1 min. The heat capacity decreased rapidly as the temperature increased. The possible temperature range was limited to 120 °C, and fabric treated beyond that temperature could not be expected to have thermal release/ storage properties. From this result, it can be seen that the MF microcapsules have a higher heat endurance level than the polyurea microcapsules. Therefore, the optimum treatment conditions were 30% concentration and 110 °C/ 1min treatment temperature/time.

Table 2.18: Effect of Cure Conditions for Thermal Properties of Treated Fabrics at 30% Microcapsule Concentration Condition by SP [141]

Temp. ℃/time, min	T_m, ℃	DH_f, J/g	T_c, ℃	DH_c, J/g
100/2	27.866	5.323	21.966	4.422
110/1	27.333	7.651	20.633	7.509
120/1	31.466	3.150	21.966	1.266
140/1	27.466	0.794	20.652	0.334

Launderability of treated fabrics: Table 2.19 shows the changes of thermal properties according to repeated launderings. Heat capacity decreased as laundering times

increased. About half of the decrease occurred after the first laundering, and small decreases occurred after five launderings. It appears that, unavoidably, capsules fall of the fabrics because of friction during launderings. The SEM results before and after launderings show that the surface of the fabric before laundering is fully covered with the coating mixture, but the coating after launderings has peeled off and there are sparsely bonded coating materials in the intersections of the yarns.

Table 2.19: Changes in Thermal Properties of Treated Fabrics After Repeated Launderings Under The Condition of 30% Concentration and 110 °C/1 min by SP [141]

Laundering times	T_m, °C	DH_f, J/g	T_c, °C	DH_c, J/g
0	27.333	7.651	20.633	7.509
1	28.266	3.923	21.166	3.603
5	27.600	3.768	21.300	3.423
10	27.600	1.051	21.166	0.676

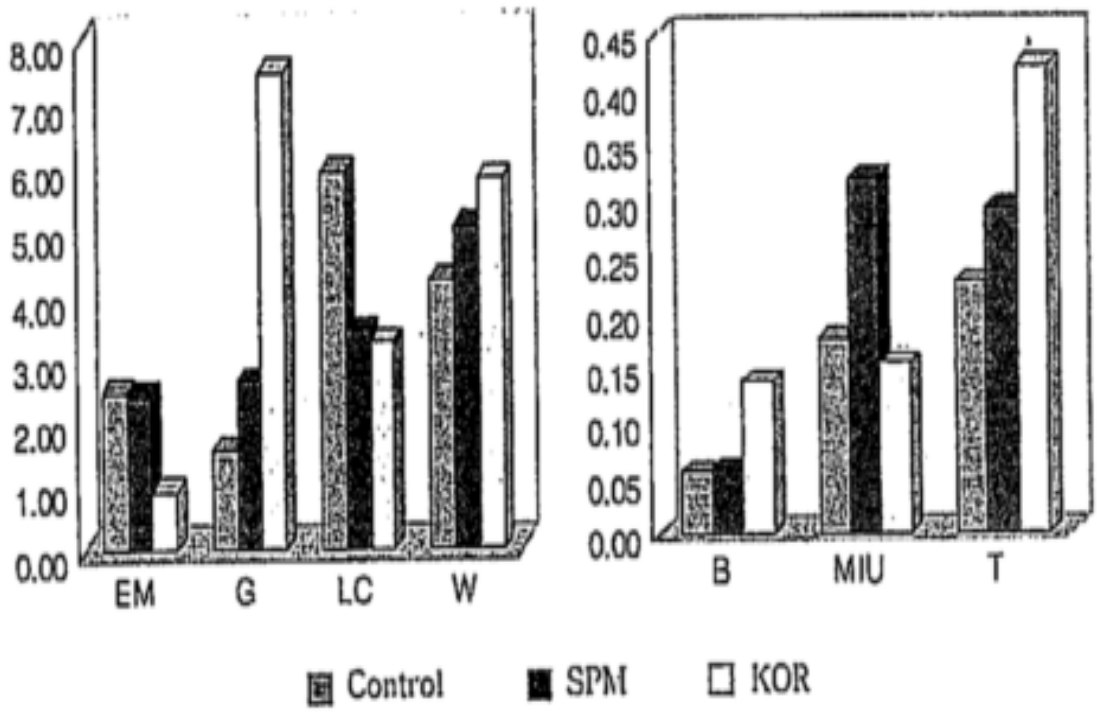


Fig. 2.82: Mechanical Properties of Polyester Fabrics Treated with Different Coating Methods at 30% Concentration and 110 °C/ 1 Minute [141]

Mechanical properties: compared with untreated fabric, the elongation of maximum load (EM) of the SP fabric decreased slightly from 2.470 to 2.426% (Fig. 2.82). Changes in tensile properties were less when the fabric treated by SP than by KOR. Shear stiffness (G) had the highest value, 7.462 gf.cm^2/cm, when the fabric was treated by KOR. Linearity of compression (LC) was highest in the untreated fabric (5.914) and lowest in the KOR fabric (3.250). Bending rigidity (B) of the SP fabric

decreased compared with KOR fabric to 0.137 gf.cm^2/cm for KOR and 0.058 gf.cm^2/cm for SP.

These results reveal that the KOR fabric is stiffer and less easily changeable to shear direction. The coefficient of friction (MIU) of the KOR fabric (0.153) was lower than the SP fabric (0.320) because the KOR, which was fully spread on the surface of fabric, was smoother than the SP, which was spread as dot shapes.

Hygroscopic properties and air permeability: Table 2.20 shows the results of hygroscopic properties and air permeability of polyester fabrics treated with the different adhesive methods. Moisture content of untreated specimen was 0.32%; on the other hand, those of the SP and KOR specimens were 0.42% and 0.43%, respectively.

Table 2.20: Hygroscopic Properties and Air Permeability of Fabrics Treated with Difference Adhesive Methods Under Conditions of 30% Concentration and 110 °C/ 1 min. [141]

Physical Properties	**Hygroscopic Property, %**		**Air permeability, Kpa s/m**
	Moisture content	Moisture regain	
Untreated	0.32	0.47	0.50
SPM	0.42	0.71	1.55
KOR	0.43	0.77	5.64

Compared with the SP fabric the KOR fabric had higher air moisture content, and the moisture regain of the untreated specimen was 0.47%, but those of the SP and KOR fabrics were 0.71, and 0.77%, respectively. The KOR fabric had the highest values of the moisture content and regain due to the hydrophilic binder, which multiplied moisture absorption in the hydrophilic polyester fabric. The values of the SP and KOR fabrics were 1.55 Kpa s/m and 5.64 Kpa s/m, respectively. The higher the resistance, the lower the air permeability, so the air permeability of the KOR fabric was smaller than that of the SP fabric. The higher the resistance, the lower the air permeability, so the air permeability of the KOR fabric was smaller than that of the SP fabric.

In conclusion; the purpose of the study is to synthesize MF microcapsules, which are considered to be more durable, and to compare the properties of the KOR and SP coating processes. To accomplish this, Kyeyoun C and Gilsoo C's [141] in 2004 analyzed the size, shape, and efficiency of microcapsules containing octadecane. To determine the proper adhesive method, the fabrics were coated by SP and KOR, and

thermal storage/ release properties, launderability, and mechanical and physical properties are evaluated.

The mean diameter of microcapsules ranges from 1 to 1.5 μm, and their shape is spherical according to SEM. DSC confirms the core content and encapsulation efficiency. The optimum combinations of concentration and temperature/ time to obtain the best thermal storage and release properties from microcapsules were found out as 30% and 110 °C/ 1min.

The thermal properties of treated fabrics increase as microcapsule concentration increases, but there is no big difference between the two adhesive methods despite the different add-ons. Thermal properties of the treated fabrics decrease after five launderings. The mechanical properties, bending, and shear rigidities of the KOR fabrics are the highest, which means the coated fabric becomes stiffer and harder because the coating is fully spread by KOR. The SP fabrics show higher air permeability and lower moisture absorption than that of the KOR fabrics.

As a result of this study, it was found out that the SP was more effective at yielding better hand and at the same time a better relative heat content efficiency than KOR.

The design and development of a functional textile providing ability to dynamic heat regulation next to the skin have attracted more and more attention in recent years [167]. Number of attempts in this field is extensive parallel to the researches in electronics, several solar energy-based systems, buildings, etc. However, the successful applications are limited and still under investigation. A remarkable group of them concerns with the manufacture of microcapsules so that spherical bi-component particles consist of shells and surrounded core material [168-174].

Phase change materials (PCMs) have been applied to the textiles in a variety of processes to improve thermal comfort of end-use products, due to their heat storage capacities. Coating, lamination, finishing, melt spinning, bi-component synthetic fiber extrusion, injection molding, foam manufacturing are some of the convenient processes for PCMs' incorporation into the structure. Well-known PCM are linear chain hydrocarbons known as paraffin waxes (or n-alkanes), hydrated salts, polyethylene glycols (PEGs), fatty acids and mixture or eutectics of organic and non-organic compounds. PCMs have also been used as a core material in the

microcapsule production, the prior stage of aforementioned processes for the fabrication of thermo-regulated fibers, fabrics, coatings or foams [175-177].

Microcapsule utilization in textile goods is advantageous since the encapsulation prevents PCM dispersion in the structure, reduces evaporation and reaction of PCMs with the outside environment, provides an increased heat-transfer area and a constant volume, and alloys an easy application without affecting other textile properties and normal fabric-care. In-fiber incorporation of microcapsules, for instance, could be achieved by loading the fiber with 5-10% of microcapsules, and thus, PCM could be permanently locked with the fiber exhibiting normal properties of drape, softness, and strength without a need of subsequent fiber processing; or washing durability of a functional cotton fabric on which the microcapsules were applied by a printing paste also including small content of acrylic binder, which was ensured up to 15 times.

Microcapsules are defined with the parameters such as particle diameter, thickness of shell, thermal capacity and conductivity, durability, etc. Thickness of particle walls may be less than 1 μm, and particle sizes vary within the range of less than 1 μm to more than 300 μm depending on the method of encapsulation, typically 20-40 μm in diameter. PCM content of a capsule may be up to 80-85% [178-182].

Microcapsule production may be achieved by means of physical or chemical techniques. The use of some techniques has been limited to the high cost of processing, regulatory affairs, and the use of organic solvents, which are a concern for health and the environment. Physical methods are mainly spray drying or centrifugal and fluidized bed processes, which are inherently not capable of producing microcapsules smaller than 100 μm. The most suitable chemical process are associated with the simple or complex coacervation and interfacial (or in situ) polymerization techniques. The simple or complex coacervation is a colloidal process in which the core material in dispersed form is added to the polymer solution, and the mixture is then suspended in an aqueous phase containing a surface-active agent. Microencapsulation of both oily and water-soluble actives is possible using oil-in-water and water-in-oil techniques. As oil-in-water coacervation is more straightforward, it is widely used in the industry. Encapsulation of paraffin waxes by complex coacervation was succeeded to attain a high energy storage /release capacity

of about 145-240 J g^{-1} identifying a good potential as a solar energy storage material [183]. The main limitation of this approach is the difficulty in scale up of the process.

In situ polymerization generally involves bringing together two immiscible liquids, e.g. water and organic solvent, respectively; containing complimentary, direct-acting, organic intermediates that will react with each other to establish a solid pre-condensate [169,175,176,181,184-192]. Condensation polymers are usually formed by the stepwise intermolecular condensation of reactive groups. The structural units of condensation polymers are usually joined by inter-unit functional groups. The in situ processes have the ability to yield microcapsules with the best quality in terms of diffusion-tightness of their walls and of a size ranging between 5 and 100 μm. Suitable polymers such as a polyamide, polyester, polyurethane, poly-urea, or like substances, can be formed from resin intermediates or monomers.

2.9. The Benefits of Microcapsule Usage in Aromachology

Pure fragrance compounds and essential oils have been used traditionally in folk medicine for a long time. It is discussed nowadays because of its viable holistic pharmaceutical effects and the trend back to natural drugs and therapies in medicine. The term aromatherapy was coined in the late 1920s by the French cosmetic chemist R.M. Gattefosse, who noticed the excellent antiseptic properties and skin permeability of essential oils [193]. Dr. G. Bauchbauer, a modern aroma therapist of renown, has proposed the following definition of the word aromatherapy: therapeutic uses of fragrances which at least mere volutilize to cure and to mitigate or cure diseases, infection and indisposition by means of inhalation alone [194].

The term aromachology [205] was coined in 1982 to denote the science that is dedicated to the study of the interrelationship between psychology and fragrance technology to elicit a variety of specific feelings and emotions – such as relaxation, exhilaration, sensuality, happiness and well-being – through odours via the stimulation of olfactory pathways in the brain, especially the limbic system [195]. The difference between aromatherapy and aromochology is difficult to describe definitely and succinctly. Notwithstanding the evident relationship between then, they have different research methods and research directions. Regrettably, in the scientific world, the definition of aromatherapy has not as yet been made clear.

The development of aromatherapy phenomenon after 1980 diversified along four basic avenues [196]: Medical and holistic medical aromatherapy as practiced in France, popular and esoteric aromatherapy as found in publications in all western societies, aromatherapy applied during massage as practiced mainly in Great Britain, and the scientific study of fragrances as encouraged by the Fragrance Research Fund.

During the past ten years, a considerable amount of research has been conducted in the United States, Europe and Japan to measure not only the effects of fragrance upon feeling, moods and emotions, but also upon several areas response [197]:

Electrical activity in the brain, physiological parameters such as the heart rate and skin conductance, cognitive functions and voluntary and involuntary behavior, Belachie determined the effectiveness of 42 essential oils against the 12 most common pathogenic microorganisms through an extensive series of experiments. An "Aromatic Index" was introduced, which characterized the overall effectiveness of the investigated essential oils against all pathogens studied. He found that the essential oils with a higher Aromatic Index could effectively prevent Escherichia coli, Proteus morgani, Candida albicans, Staphylococcus aureus etc.

Torii et al. studied the contingent negative variation (CNV) and the physiological effects of odour in humans [198]. They found that the presentation of jasmine odour caused a significant increase in the CNV measured at the frontal and left central sides of the cortex, while a lavender odour caused a significant decrease. Taking a nap and drinking a cup of coffee changed the CNV in the same direction; an increase in the CNV was interpreted as signaling stimulation and decrease as signaling relaxation.

Bauchbauer's team studied the effects of single aroma chemicals and essential oils inhale by mice [199]. They investigated 44 chemicals and essentials with ascribed sedative effects on humans. The studies showed that lavender oil, its main constituents, linalool and linalyl acetate, as well as neroli oil, benzaldehyde and East Indian sandalwood oil, decreased the motility of untreated mice by 40-78%, and compared with the control group. Torii investigated the effects of odours upon the skin's potential level (SPL) [200]. SPLs are related to mental perspiration, and corresponded well with the arousal level of the subject; -40 MV upon awakening, -60 mV at the time of excitement, and near zero mV during sleep. Measurements of the SPL via the contingent negative variation (CNV) clearly showed the variation of SPL

in parallel with the level of activity of the sympathetic nervous system. Torii reported that the scent of camomile oil produced sedative effects, while the scent of jasmine oil was stimulating.

Nasel performed Xe-computer-tomographic studies on eight healthy volunteers aged between 20 and 30 years old, and one tested anosmatic woman, with a view to observing the cerebral blood flow upon inhalation of 1,8-cineole [201]. In all cases, the CBF of these subjects increased when inhaled this compound. The anosmatic woman reacted in exactly the same way. It showed that increased CBF could not be the result of a reflectoric event. In addition, the concentration of 1,8-cineole in the blood was determined. Resorption was very fast, as could be shown during the period from 4 to 20 minutes by an almost linear increase of the 1,8-cineole concentration up to a maximum value of about 275ng/ml serum. When the inhalation was stopped, the concentration of this chemical in venous blood dropped immediately. It showed that this essential oil was very safe for the human body.

Many methods have been applied in aromatherapy research in order to verify the so-called healing effects of aroma chemicals and essential oils. It is very difficult to separate the psychological from the pharmacological. In fact, more research work is needed.

Effects of aromatherapy:

Lavender is the most used and most versatile of all the essential oils. It is very useful oil, especially when symptoms are due to a nervous problem [202]. Many research works have confirmed the effects of lemon, camomile, rose, cardamom, clove, and jasmine fragrance oils on human. The sedative effects for the pharmaceutical and emotional effects of essential oils are listed in the Tables 2.21, Table 2.22, Table 2.23 and Fig. 2.83.

Microcapsules and aromatherapy textiles:

The fragrance compound and the essential oil are volatile substances. The most difficult task in preparing the aromatherapy textile is how to prolong its lifetime of odour. Microencapsulation is an effective technique to solve this [203,204].

Microcapsules are minute containers that are normally spherical if they enclose a liquid or gas, and roughly of the shape of the enclosed particle if they contain a solid. It can be considered as a special form of packaging, in that particulate matter can be individually coated for protection against environment and release the volatile

substance from the capsule as required. This property has enabled microcapsules to serve many useful functions and find applications in different fields of technology [205]. For example, the storage life of volatile compound can be increased markedly by microencapsulation [206].

The key to aromatherapic textile is how to make microcapsules of fragrance compounds and essential oils without omitting any ingredient in order to ensure its pharmaceutical effects. In addition, using a low-temperature polymer binder to attach a perfumed microcapsule to the surface of the textile is also an important part of preparing an aromatherapic textile. At the same time, durability in laundering and a soft handle should be carefully considered [207].

Although there are many effective approaches to microencapsulation for decreasing fragrance-release, cyclodextrins are the best regarding safety to the human skin irritation, no skin sensibilisation and no mutagenic effect [208].

The uses of aromatherapy textile are diverse. Interior textiles such as sheets, quilt-covers, curtains, carpets and bed-gowns are suitable for the attachment of lavender, camomile, citrus or cinnamon microcapsules, which are good for hypnogenesis and eliminating fatigue. Patients suffering high blood pressure feel sedation when they use a pillow made of fabric treated with lavender, basil, and lemon or fennel microcapsules. The tired office clerk wearing clothing with a scent of lemon, rose, or jasmine oil may find his work efficiently improved. Meanwhile, it is convenient for dermatosis sufferers to be cured with the aid of underwear containing killing gem fabric. Perfumed toys make it easier for children to get closer to nature. Generally speaking, varied perfume fabrics create good opportunities for customers to make the “cocooning” environment they prefer to live in.

Arometraphy is increasingly popular as one of many approaches to healing with natural substances, which are favored by the public, and make it possible for the individual to attempt self-therapy at home. As close friends of humans, textiles can make aromatherapy easy where they are needed. Microencapsulation can effectively control release rate of the fragrance compounds and essential oils as required, which ensures the storage life of volatile substances.

Various products may be chosen such as fibers, fabrics, non-fabrics and garments to enjoy the pharmaceutical and emotional effects of aromatherapy textiles. It is for sure

that aromatherapy and aromatherapic textiles are the fist choice for people who want to keep healthy in their daily life, and these textiles will become a fashion in the near future [209].

In this thesis, coconut oil (Myritol 318) was used as one of the active ingredients within the microcapsules together with vitamin E. Coconut oil has a lot of benefits.

2.9.1. Specifications of Coconut Oil

Coconut oil has been used for centuries as a vital source of food for health and general well being in traditional communities of tropical regions. Coconut oil, also known as coconut butter, is tropical oil extracted from copra (the dried inner flesh of coconuts) with many applications. Coconut oil constitutes seven percent of the total export income of the Philippines, the world's largest exporter of the product. Coconut oil was developed as a commercial product by merchants in the South Seas and South Asia in the 1860s.

Physical properties of coconut oil: Coconut oil is a fat consisting of about 90% saturated fat. The oil contains predominantly medium chain triglycerides, with 86.5% saturated fatty acids, 5.8% monounsaturated fatty acids, and 1.8% polyunsaturated fatty acids. Of the saturated fatty acids, coconut oil is primarily 44.6% Lauric acid, 16.8% Myristic acid and 8.2% Palmitic acid, although it contains seven different saturated fatty acids in total. Its only monounsaturated fatty acid is oleic acid while its only polyunsaturated fatty acid is linoleic acid. Unrefined coconut oil melts at 20-25 °C and smokes at 170 °C (350 °F), while refined coconut oil has a higher smoke point of 232 °C (450 °F).

Table 2.21: The Pharmaceutical Effects of Essential Oils [207,208]

Effects	**Essential Oil**
Sedation	Mint, Onion, Metasequoia
Coalescence	Pine, Clove, Lavender, Onion, Thyme
Diuresis	Pine, Lavender, Onion, Thyme, Fennel, Lemon, Metasequoia
Facilitating Menses	Pine, Lavender, Mint, Rosemary, Thyme, Basil, Chammomile, Cinnamon, Lemon
Dismissing sputum	Onion, Citrus, Thyme, Chammomile
Allaying a fever	Ginger, Fennel, Chammomile, Lemon
Hypnogenesis	Lavender, Oregano, Basil, Chammomile
Curing Hypertension	Lavender, Fennel, Lemon, Ylangylang
Be good for stomach	Pine, Ginger, Clove, Mint, Onion, Citrus, Rosemary, Thyme, Fennel, Basil, Cinnamon
Diaphoresis	Pine, Lavender, Rosemary, Thyme, Chamomile, Metasequoia
Expelling wind	Ginger, Clove, Onion, Citrus, Rosemary, Fennel, Lemon
Losing weigh	Onion, Cinnamon, Lemon
Relieving pain	Vanilla, Lavender, Mint, Onion, Citrus, Rosemary, Chamomile, Cinnamon, Lemon
Deloxification	Lavender
Curing diabetes	Vanilla, Onion, Chamomile, Lemon
Stopping diarrhea	Vanilla, Ginger, Clove, Lavender, Mint, Onion, Oregano, Rosemary Thyme, Chamomile, Cinnamon, Metasequoia
Curing flu	Pine, Lavender, Mint, Onion, Citrus, Rosemary, Thyme, Chamomile, Cinnamon, Metasequoia
Curing rheumatism	Lavender, Onion, Citrus, Rosemary, Thyme, Metasequoia
Urging sexual passion	Pine, Ginger, Clove, Mint, Onion, Citrus, Rosemary, Thyme, Fennel, Relieving Spasm Cinnamon
Promoting appetite	Clove, Lavender, Mint, Onion, Citrus, Rosemary, Fennel Basil, Chamomile, Cinnamon, Lemon, Metasequoia
Relieving cough	Rosemary

Coconut oil has a long shelf life compared to other oils, lasting up to two years due to its resilience to high temperatures. Coconut oil is best stored in solid form - i.e. at temperatures lower than 24.5 °C (76°F) in order to extend shelf life. However, unlike most oils, coconut oil will not be damaged by warmer temperatures.

One of the main reason using coconut oil as active ingredient in the capsules in this thesis is that it has longer shelf life than the other oils. Around two years it can resists to environmental conditions and high temperature. This is very important characteristic to have long-life microcapsules, which have long shelf life active ingredient inside.

Table 2.22: The Sedative Effects/or Emotion of Essential Oils [194]

Emotion	Essential Oils with The Sedative Effects
Anxiety	Benzoin, Lemon, Chamomile, Rose, Cardamon, Clove, Jasmine
Stimulation	Camphor, Balm Oil
Anger	Chamomile, Balm Oil, Rose, Ylangylang
Wretchedness	Basil, Cypress, Mint, Patchouli
Allergy	Chamomile, Jasmine, Balm Oil
Distrustfulness	Lavender
Tension	Camphor, Cypress, Vanilla, Jasmine, Balm Oil, Lavender, Mint, Rose
Melancholy	Basil, Lemon, Chamomile, Vanilla, Jasmine, Lavender, Mint, Rose
Hysteria	Chamomile, Balm Oil, Lavender, Jasmine
Mania	Basil, Jasmine, Pine
Desolation	Jasmine, Pine, Patchhouli, Rosemary

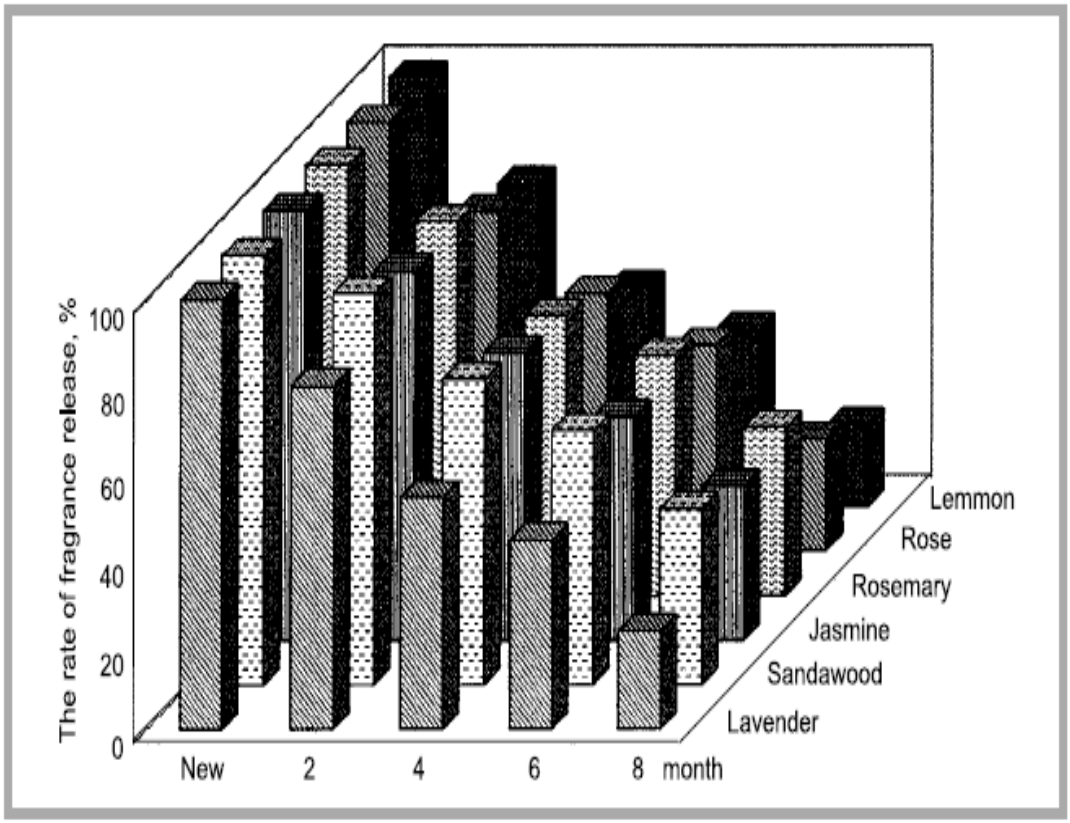


Figure 2.83: The Rate of Fragrance-release From Microcapsules [194]

Table 2.23: Sensorial Evaluation of Scent Intensity: + + + + + Express Very Strong, + + + + Express Strong, + + + Express Common, + + Express Weak, + Express Very Weak [194]

Fragrance	**Scent Intensity**					
Substance	**5 days**	**10 days**	**15 days**	**20 days**	**25 days**	**30 days**
Rosemary	+++++	+++++	+++++	+++	+++	++
Lavender	+++++	+++++	+++	++	++	+
Jasmine	+++++	+++++	++++	+++	++	++
Lemon	+++++	+++++	+++	++	+	+
Sandalwood	+++++	+++++	++++	+++	+++	++

Chemical properties of coconut oil: Among the most stable of all oils, coconut oil is slow to oxidize and thus resistant to rancidity. Epidemiological studies have been performed on tropical cultures that get a majority of their caloric intake from coconut oil. The most popular study was conducted in the early 1980s on the Polynesian islands of Pukapuka and Tokelau - two cultures relatively untouched by western food at the time. Both cultures had a high intake of saturated fat, with one of the island's population consuming 63% of their caloric intake from coconut. The people were found to be very healthy, and the authors of the study concluded: "Vascular disease is uncommon in both populations and there is no evidence of the high saturated fat intake having a harmful effect in these populations. However, these results may not necessarily be applicable to other populations, nor can the fact that these people's high saturated fat content be determined to be the cause of their good health. Being untouched from western culture could have resulted in islanders living an active lifestlye, explaining the positive health observation.

Manufacturing: Coconut oil is used in volume quantities for making margarine, soap and cosmetics. Hydrogenated or partially-hydrogenated coconut oil is often used in non-dairy creamers, and snack foods. Fractionated coconut oil is also used in the manufacture of essences, massage oils and cosmetics

Cosmetics and skin treatments: Coconut oil is excellent as a skin moisturizer. A study shows that extra virgin coconut oil is as effective and safe as mineral oil when used as a moisturiser, with absence of adverse reactions. Coconut oil can also help in healing Keratosis pilaris by moisturising the affected area. The coconut oil should be applied in the shower, and may cause the KP bumps to disappear. In India and Sri Lanka, coconut oil is commonly used for styling hair, and cooling or soothing the head (stress relief). People of coastal districts of Karnataka and Kerala bathe in warm

water after applying coconut oil all over the body and leaving it as is for an hour. It is suggested by elders that this ritual must be done at least once in a week, to keep body, skin, and hair healthy.

The healing properties of coconut oil:

- Coconut oil is antiviral, antifungal (kills yeast too) and antibacterial. It attacks and kills viruses that have a lipid (fatty) coating, such as herpes, HIV, hepatitis C, the flu, and mononucleosis. It kills the bacteria that cause pneumonia, sore throats, dental cavities, urinary tract infections, meningitis, gonorrhea, food poisoning, pneumonia, and many, many more bacterial infections. It kills the fungus/yeast infections that cause candida, ringworm, athlete's foot, thrush, jock itch, diaper rash and more.

- Coconut oil is called the "low fat" fat. It actually acts like a carbohydrate in that it is quickly broken down in the liver and used as quick energy. It is NOT stored like other fats. It boosts one's energy and endurance. Many athletes use it blended into their drinks. It also supports thyroid function and increases your metabolism. It is great if people want to lose weight.

- Coconut oil improves digestion and absorption of fat- soluble vitamins, minerals (especially calcium and magnesium), and amino acids. It improves the body's use of blood glucose and improves insulin secretion and absorption (great for type II diabetes). In fact, many diabetics (type I and type II) use it to reduce their symptoms. One's risk of diabetes decreases with regular use of coconuts and coconut oil.

- Coconut oil helps the body heal and repair faster. It aids and supports immune function, protecting us from a variety of cancers.

- Coconut oil, contrary to much hubbub, is good for your heart. It keeps our blood platelets from sticking together (and causing dangerous clots). Regular users of coconut oils have a much lower chance of atherosclerosis (clogging of the arteries), arteriosclerosis (hardening of the arteries), and strokes. Coconut oil can lower your blood pressure. Coconut oil is a natural antioxidant. It protects the body from free radical damage and prevents premature aging and degenerative diseases.

- Finally, coconut oil is the best massage oil on the planet. It forms a barrier against infections, softens and moisturizes your skin, and prevents wrinkling,

sagging, and age spots. It promotes healthy hair and complexion, protects from any damaging UV rays.

2.9.2. Specifications of Vitamin E: α-tocopherol

In the study of Sang-Ho Y, et al., [210], among the various Vitamin E categories, α-tocopherol (α-TP) is a representative anti-oxidant that dissolves in oil. Alpha –TP has been used as a food additive to provide its antioxidant role and also as a functional material to prevent cardiovascular diseases and cancer. However, the utilization of beneficial effects of α-TP is limited because this compound is labile to heat and oxygen, then irreversibly converted to quinone via epoxide formation when is exposed to heat and oxygen. In addition, the lipophilic α-TP does not dissolve in water and thus should be assisted by surfactant or emulsifier to increase bioavailability. Typical dissolving method of lipophilic compounds is to generate an emulsion by homogenizing the mixture of targeted material and emulsifier in water, but the resulting vehicle size is generally too large and cracking and creaming occur during storage. These impediments to α-TP application can be partially overcome by applying microencapsulation technology to protect α-TP from unfavorable environment and to solubilize it in aqueous environment.

Vitamin E is the generic term referring to eight naturally occurring isomers, a family of four tocopherol (alpha-, beta-, gamma- and delta-) and four tocotrienol (alpha-, beta-, gamma-, and delta-) isomers varying to the extend in which the chromanol ring is methylated.

In this thesis, α-tocopherol was used together with Myritol 318 coconut oil as active ingredient in the core of the microcapsules. Because, α-tocopherol is the most biologically active form of Vitamin E (over 10 times more potent than tocopherol acetate) and is highly effective as an antioxidant and free radical scavenger (tocopherol acetate is mainly effective as an antioxidant to formulation, not to the skin). α-tocopherol slows down the aging process while protecting and moisturizing the skin. However, when incorporated into cosmetic formulations in its naked form, Vitamin E oxidizes and loses its original activity. Therefore, microencapsulation process is extremely needed. The microcapsule protects α-tocopherol from oxidation and maintains its original activity after incorporation into cosmetic formulations.

Vitamin E is widely used in dermatological and cosmetic products due to its beneficial effects on the appearance of healthy skin. Vitamin E is an essential fat-soluble vitamin and acts solely as a membrane bound antioxidant.

One of the typical characteristic of Vitamin E is that it may also simply characterized by its chromatographic behavior. That's why vitamin E was used in this study to obtain quantitative values under gaschromatogram.

For many years, vitamin E's main claim has been as a moisturizer to relieve dry skin and indirectly aid in the concealment of wrinkles and facial lines perceived as characteristic of aging skin. Extensive studies conducted over the past 10 years with topically applied vitamin E have revealed additional significant benefits, most important of which are:

- Inhibition of collagense formation: During aging processes total protein kinase C expression in human fibroblasts increases up to 8 fold. This event induces collagenase over-expression followed by increased collagen degradation. α-tocopherol is able to protect the skin aging by decreasing the level of collagenase expression, which is induced by aging and environmental insults. Topical use of vitamin E induced smoothing of fine lines and wrinkles in a sensitive area of the face.

- Enhancing the level of epidermal and dermal antioxidants: This effect involves the up-regulation of a network of enzymatic and non-enzymatic antioxidants.
- Photo-protective action: Exposure to UVA and UVB reduces the level of α-tocopherol in the skin. It was shown that topical vitamin E inhibits the formation of cyclobutane pyrimidine photoproducts on the skin through a combination of antioxidant and UV absorptive properties. Increasing doses of vitamin E reduced UVB-radiation-induced skin cell death and apoptosis.
- Antioxidant activity: Topical and/or systemic application of α-tocopherol can support physiological mechanism to maintain or restore a healthy skin barrier. Vitamin E has the potential to reduce DNA damage and inhibit malignant transformation through its antioxidant function. Vitamin E significantly increases the activity of antioxidant enzymes, such as super oxide dismutase, and decreased lipid peroxide.

- Protection against environmental pollutants: The stratum corneum, the permeability barrier of the skin, represents a sensitive target for ozone-induced oxidative stress and of vitamin E depletion. Repeated low level of ozone exposures resulted in cumulative oxidative effects in the stratum corneum. It has been found that damage to the cutaneous lipids caused by ozone exposure is an effect that can be attenuated by vitamin E application.
- Wound healing: This is a complex process involving interactions among a variety of different cell types. The normal wound repair process consists of three phases-inflammation, proliferation, and remodeling- that occur in a predictable series of cellular and biochemical events. Vitamin E inhibits the inflammatory response, reduces the number of fibroblasts (cells that multiply at the site of chronic inflammation) and retards collagen accumulation at the wound site.
- Anti-inflammatory activity: In an evaluation of the anti-inflammatory effect of vitamin E, topical vitamin E reduced the severity and duration of croton oil dermatitis in rabbits.
- Moisture effect: The influence of vitamin E on stratum corneum hydration was tested in O/W and W/O emulsions. In the W/O emulsion, 2.5%, 5% and 7.5% vitamin E were compared. With both types of emulsions, vitamin E increased stratum corneum hydration significantly. There is evidence of an enhanced water-binding capacity after treatment with vitamin E. The concentration of vitamin E is important for its hydrating effects. The optimum concentration is indicated at 5%. Vitamin E acts as a moisturizer regulating the movement of water in skin. Hydrated skin has comparatively wider lines with a smoother appearance and is less sharply demarcated.
- Regulation of skin proliferation: α-tocopherol has been found to negatively regulate proliferation of human skin fibroblasts thereby reducing the signs of aging, as cell proliferation is an important event in the aging process.
- Synergistic combination: Extensive studies showed that glycolic acid could strongly potentiate the antioxidant action of α-tocopherol. This suggests the advantage of combining alpha-glycolic acid with these antioxidants in skin-designed preparations, both to improve penetration and availability of antioxidants to epidermal layers and to enhance their protective potential. The best photo protective effect was achieved from the combination of topical vitamins E and C.

The microencapsulation techniques, such as spraying drying, spray chilling, extrusion, coacervation, co crystallization, and freeze-drying; have been widely applied in the food industry for encapsulating vitamins, minerals and other sensitive ingredients. Solvent extraction is another way to produce nutrient delivery system (NDS) but this method uses toxic organic solvents, causes environmental pollution, and generates high processing cost. Spray drying seems to be an ideal method for food application but heat-labile core materials can be severly damaged during heat-involving manufacturing process.

In the study of Sang-Ho Y, Young-Bin S, Pahn-Shick C, Hyeong G.L; sodium alginate was used as coating material for producing microcapsule, and optimal microencapsulation yield of α-tocopherol was obtained. Furthermore, in vitro releasing property of core material, α-tocopherol, was investigated to show applicable potential of alginate as an effective nutrient delivery carrier.

Encapsulation yield of α-tocopherol: the encapsulation yield of α-tocopherol was determined, following the methods of Gohel and Amin and Jee et al. with some modifications. The coating material structure of microcapsule was completely destructed by following procedure: fifty milligrams of prepared microcapsules was accurately weighed and dispersed in 50 ml of ethanol. This dispersion was agitated at 700 rpm for 12 h, and then ultrasonic-treated twice for 20 min with 10-min interval. The supernatant after centrifugation at 1800X g for 10-min was obtained from the disintegrated microcapsule dispersion, and the amount of α-tocopherol was quantified by measuring UV absorbance at 285 nm. The actual yield of microencapsulation was calculated using the equation below:

Yield (%) = (Actual amount of α-TP in the microcapsule / Theoretical amount of α-TP in the microcapsule) X 100 (2.10.)

In vitro α-TP releasing test of the sodium alginate (SA) based microcapsules was performed. The SA microcapsule released 28.8% of α-TP when exposed in the stimulated gastric fluid (SGF, pH 1.2) for 24 h. In the simulated intestinal fluid (SIF, pH 7.4), the amount of released α-TP (81.5%) was significantly greater than that in the SGF. The duration time required for releasing 50% ($T_{50\%}$) and 70% ($T_{70\%}$) of α-TP from the SA-microcapsule were calculated to be 3.8 and 12.3 h, respectively. From these results, it was suggested that SA microcapsule would be structurally

resistant against acidic environment, and it would rapidly release core material under mild alkali condition.

2.10. Odour Measurement in Textile Industry

A branch of metrology called odorimetry deals with odour measurements. Odour is an important quality of textile objects, especially those that influence odour formation inside rooms and in the vicinity of human beings. It is important not only for the net curtains, drapes, linens or garments, but also for carpets, covers, tents, upholstery fabrics etc. Odour is also measured in many other industries, such as the chemical, food, oil and motor industries, as well as in animal breeding and environmental protection. Until recently the only methods used were organoleptic methods, based on human olfactory sensations. For a number of years attempts have been made at establishing a scientific objectivity of this measurement by constructing a variety of technical devices. Following the first enthusiastic reports about the possibility of measuring odour, it appeared that the problem had not in fact been solved. The evidence of this was a lack of correlation between the indications of the devices and the assessment of experts, the so-called sniffers. At present, there are number of well thought-out and mature constructions of measuring equipment units that yield comparable, numerical results; however most of them still require the direct participation of human in the measurement. This individual's task is to use their olfactory perception as an odour detector.

A different scale of intensity is also used. It is an ordering six-degree scale, in which particular degrees are ascribed, the following denotations of odour:

0 = imperceptible
1 = very weak
2 = weak
3 = perceptible
4 = distinct
5 = intensive, very distinct.

Aggressiveness is related to the discomfort of inhaling odour perceived as unpleasant. This is assessed according to the multi-degree ordering scale. Ammonia of different concentrations is sometimes used for comparison. This quantity is most

often determined during measurements associated with the assessment of the effect or large breeding farms [211] and textile factories (especially finishing mills) [212] on the environment (Fig 2.84).

Type of odour is described verbally and differently in a different branch. The following words can serve as examples of such terms: ‘floral’, ‘almond’, ‘hop’, ‘caramel’, ‘foul’, ‘pungent’, ‘maize’ etc. When the more detailed characteristics of the odour must be described in scientific research, a more extensive description of the type of odour is given.

For example, to define tetrohydrofuranoids and pyranoids, the following terms have been used; ‘sweet, interesting, pleasant, similar to the odour of the orange rind’. The odour of rose-oxide, in turn, has been described as ‘very characteristic, green, penetrating, slightly resembling the odour of the rose and geranium [213].

In the perfume industry, the quality of odour is described; in standardization documents it has been evaluated (among other ways) in a six-degree scale (from zero to five). This is a notion connected with the possibility and manner of reproducing the odour of, for example, a flower. The following terms are ascribed to the particular degrees of quantity: strange (not floral), does not resemble the flower, resemble the flower to a small degree, slightly resembles to flower, is perfectly associated with the flower.

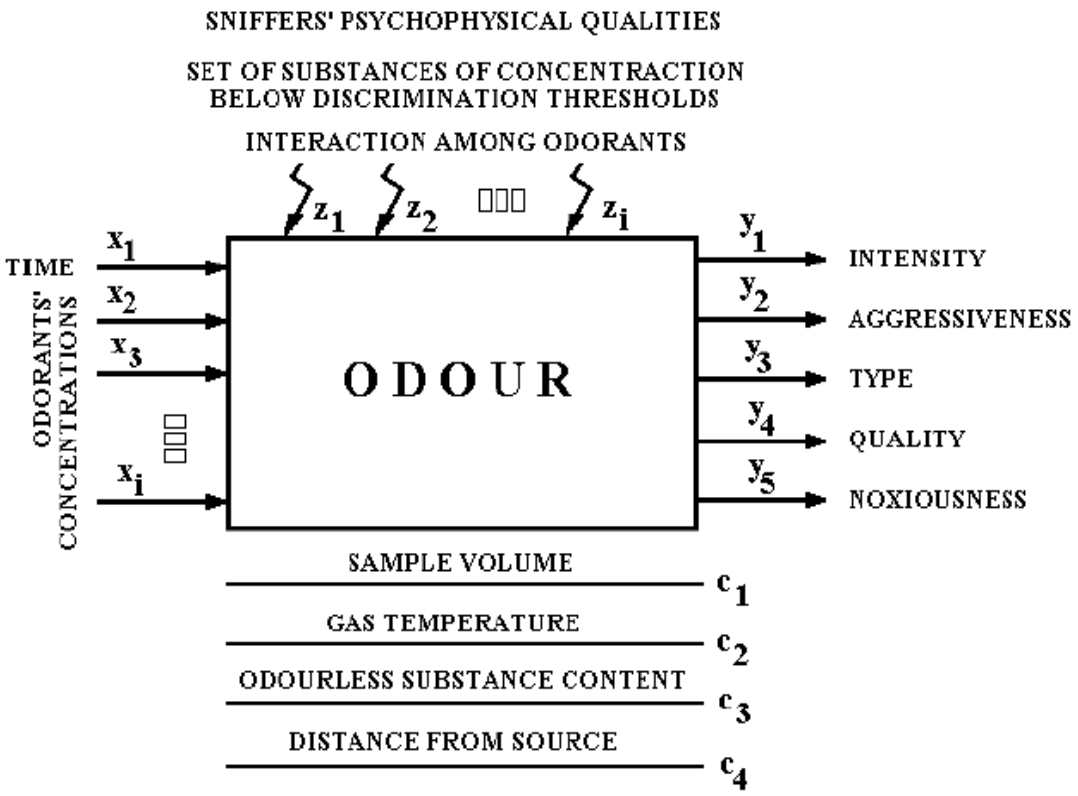


Fig. 2.84: A Qualitative Mathematical Model of Odour [214].

Odour is also described by means of a feature called hedonistic quality [214], which is related to the permissible time of exceeding the threshold concentration of the sensibility expressed, in percent, as a part of a year. Attempts at the determination of this feature are at a stage of preparation of the standard project.

There have also been attempt to measure the noxiousness of odour [215], which can also be defined as a number of complaints of a given population over a definite period of time. This feature is indirectly connected with aggressiveness, but is defined in a different manner.

Investigations carried out recently around the world lead to the common awareness that odour has fundamental influence on people's general comfort and even on their health. This influence can be as much as a positive as of a negative character. For example, the reassuring effect of lavender and the harmful influence of ammonia on human is known. This is why it is very important to create the possibility to form an appropriate odour in rooms and in the environment immediately surrounding people. This especially concerns textile products, which in the form of underwear, clothes,

bedclothes, sheets, blankets, and textile furnishing of living rooms of all kinds accompanies humans day after day without interruption.

The manufacture of aromatic fibers designed for such everyday textile products as bedclothes, apparel, curtains, and draperies appeared to be a very good solution. The Cripy 65 fiber, developed after intensive research conducted in Japan [211] and manufactured in the Mitsubishi Rayon Laboratories, can be mentioned here as an example. This hollow fiber contains flavouring extracts in its structure that yield a sufficiently intensive and durable fragrance. The aromatic substances are displaced in four longitudinal channels arranged at angle of 90 degrees around the central hollow channel. A polyester fiber manufactured at Kanebo Ltd (Fig. 2.9.6) can be and example of a fiber of opposite action, aimed at removing unpleasant odour. This fiber is applied in the production of stockings and everyday clothes. A fiber that possesses very strong fungicidal properties and at the same time is able to effectively suppress unpleasant odour is similarly offered by the Tejin Company. This fiber is manufactured as a core-crust system in which the crust consists of a co-polymer of ethylene and acrylic acid, and the core can be made, for example, of polyester. Additionally, the core contains pulverized copper. This structure possesses the possibility to the chemically assimilate the odorant, whereas the regeneration of the structure is achieved over the period of washing and drying. Aromatic substances can also be placed in microcapsules dispersed uniformly over the cross-section area, which forms such durable connections that the flavour ceases only to an unimportant degree and over long periods of use.

Odour is also a very important element of technological processes in the textile industry. Many finishing departments exist, in which the so-called open processing methods have been used up to now; these are characterized by the use of acetic acid, formic acid and sodium hypo chlorite, which all cause sharp smelling effects. A finish application of a different kind, such as antimite finishes, is an example of other processes that results in a long-lasting characteristic smell markedly distinguished by users. Smell also has marketing importance, as it is the fist feature estimated after entry into a shop with textile products, fabrics or clothes.

For smell estimation of raw materials and textile products and for an analysis of the efficiency of odour removal, objective measurement methods of this quality are necessary. The measure of odour, similar to the measurement of many other textile

properties, proved a very difficult and troublesome problem. The emanation of odour from fibers depends not only on their temperature but also on their humidity. The intense smell of damp wool fibers and wool products (which ceases after their drying) is well known feature. An important problem is the smell emanating from nonwoven destined as filtration insertions for protecting the upper respiratory tracts. A problem of similar or even greater importance is the odour emitted by floor coverings and furnishing materials. All tests of the above mentioned fabrics demand the necessity of temperature and humidity stabilization over the time of measurement. Odour is a feature of the volume of a given air sample, and not of the tested textile, which is only the emitted of the smell. Taking this into account, it is evident that not only is the manner in which a sample of fibers or fabrics is taken for the test very important, but also the sampling method of collecting a preset air volume at a given distance from the odour source.

Odour is a quantity whose measurement manifests the features of creative measurement. This results from the fact that there is no parametric, quantitative model of this object. Such a model may be created when the conditions for artificial, reproducible representation of human reaction to sensual stimuli are laid down. It seems, however, that in spite of considerable progress in the analysis and formation of neural networks, it will be a long time until such a model can be formed [216].

3. EXPERIMENTAL

3.1. Method

The primary aim of the thesis was to determine;

a) The role of various parameters which play active role during microcapsule production processes.

b) The proper microcapsule type and size for textile industry.

c) The proper microcapsule application processes on fabric.

d) The improvement of laundering durability with processing chitosan after microcapsule application to the fabric.

Three different sizes of microcapsules were produced in Cognis GmbH Research Laboratories in Germany. By using three different types of binder quality and two different types of application process; different recipes were prepared and these microcapsules were applied to the fabric. The microcapsule application processes on to the fabric used in this study are:

- Exhaust process and
- Foulard process.

4 different recipes were prepared in exhaust method, and 9 different recipes were prepared in foulard processes.

The microcapsule laundering durability of the fabric were examined under scanning electron microscopy (SEM) and all recipes were compared with each other in the following steps:

- Before wash
- After 1 wash
- After 5 wash
- After 10 wash

More than 1.500 SEM images were obtained to analyze the processes detailed.

The recipes that gave good result in terms of laundering durability were used in the second phase recipe implementation via chitosan lactic acid solution. The fabric treated by microcapsules via foulard process secondly was passed through the foulard once again and in this case, there was only chitosan acid solution in the foulard bath.

The laundering durability of microcapsule applicated fabrics with and without chitosan coating was analyzed by SEM and by gas chromatography. Before wash, after one wash, after five washes and after ten washes; the vitamin E and myritol oil amounts were measured by gas-chromatographic analysis, results were prepared as graphics and compared for each recipes.

3.2. Microcapsule production

The manufacturing processes of the microcapsules used in this thesis were produced with a similar system like in-situ polymerization:

a) Copolyacrylate is added in to water and stirred homogenously. Copolyacrylate is an anionic polymer is with randomly dispersed carboxyl functions. The acrylate ion (CH2=CHOO-) is the ion of acrylic acid. Acrylates are the salts and esters of acrylic acid. Acrylates contain vinyl groups, that is, two-carbon atoms double bonded to each other, directly attached to the carbonyl carbon. Acrylates are common monomers in polymer plastics, and forming the acrylate polymers. Acrylates easily form polymers because the double bonds are very reactive. Here, carboxyl functioned polymer is fully polymerized, which means no monomer is available, no contamination and as a result of this, no residual left. There is no emulsifying residual. Carboxyl polymer is also good emulsifier and dispersing agent. Therefore, no need to use any type of chemical that has emulsifying and / or dispersing functions. Melamine-formaldehyde (MF) + carboxyl polymer together form the wall membrane of the microcapsules used in this thesis. Usage proportion of carboxyl polymer: MF resin is 80:20 [217]. Another reason of using those anionic pre-polymers is that they are ideal dispersants for the oily substances and can be polymerized rather easily in a micelle form creating the polymer shell for the microcapsules. Beside that, this kind of polymer disperses nicely most substances that are insoluble in water and is easily cross-linkable to a solid shell after the droplets have reached the right size. Any type of oil is added which can be counted as active principle. In this

thesis, vitamin E and myritol oil (a kind of coconut oil) were added, also for further gas-chromatographic analysis.

b) Oil is dispersed in anionic polymer solution.

c) With the help of anionic polymer, oil does not go up and emulsified in anionic polymer solution. So, dispersing and emulsifying properties are provided with the help of anionic polymer initially added in to water.

d) At this stage, sizes of the droplets are quite big, as around 50µ.

e) To reduce the size of the droplets around 2 to 10µ; depending on where it is planned to be used; a mechanical shearing force (stirring rate by homogenizer) is applied on to the oil droplets, which is already covered by anionic polymer around it.

f) These capsules are not solid yet. We have still oily liquid and anionic polymers and they are not stabile enough.

g) Therefore, to make the microcapsules enough stabile, a cross-linking agent are added in to the reactor device and processed under 80^0C during 30 minutes.

h) The used cross-linking agent is a melamine- formaldehyde based cross-linker. Melamine-formaldehyde (MF) makes the capsule surface much stronger and harder.

i) At the end, enough stabilized microcapsule dispersion is produced in this study. The ratio of wall to content is always 75/25. By this way, the wall thickness can be calculated easily. The smaller the capsules, the thinner the wall in absolute terms.

Microcapsules' active ingredient can be released with the help of:

a) Mechanical effect or friction.
b) By enzymatic or chemical attack.
c) When wall material is solved, melt or burn.
d) If the wall material is permeable, then by diffusion.
e) pH change; wall of the microcapsules are normally not solved under the pH 6-7. However, when fabric touches the human skin, then pH decreases to 4 to 5. Therefore wall of the microcapsules are solved and the active ingredient is inside the capsules are released. (Fig. 3.1.) [218].

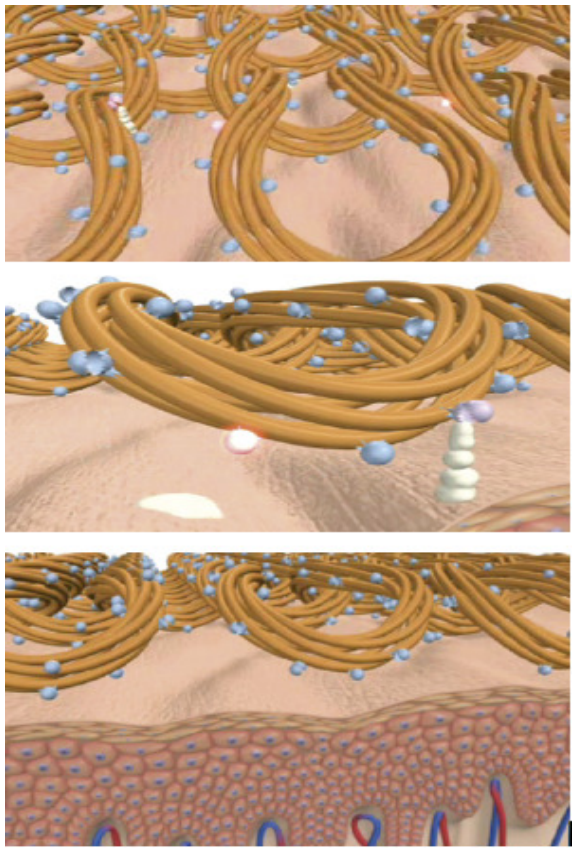


Figure 3.1: Release Mechanism of Microcapsules onto The Skin from Textile Material [218]

All above points that play active roll for the release of the active ingredients from the microcapsules are also valid for the microcapsules used in this thesis, except by diffusion. The microcapsules used in this thesis are not permeable, because a long shell-life during storage conditions as well as long product life for end-consumers are required in apparel industry. Therefore, any release by diffusion would mean that the active content of the microcapsules are already lost during the storage of the textiles. This is basically is not expected. The microcapsules in this thesis basically release its content when the shell is broken with other parameters mentioned above.

3.3. Materials Used

In this study, Myritol 318 (coconut oil)/ vitamin E blended microcapsules were used in three different mean size diameters. These capsules were applied on Supplex fabric (90% Polyamide, 10% Lycra) that is 240g/sqm. The characteristics of the materials, the capsule sizes and binder characteristics are given in Table 3.1:

Table 3.1: Capsule Sizes and Binder Types Used in This Study and Their Characteristics.

Mean Sizes of Microcapsules		**Binder Qualities Used in Different Recipes**	
Capsule Type	Capsule Size	Type	Characteristic
Capsule A	2-3 µm	C3001A	Strong binder, hydrophobic
Capsule B	8-10 µm	C3002 A	Cross linking agent
Capsule C	3-4 µm	C3003 A	Hydrophilic binder
		C3009 A	Strong binder, slightly hydrophilic

C3001A is a cross-linkable aminosiloxane; C3002A is siloxane-based crosslinker. C3001A and C3002A together form a tridimensional very wash resistant network. This is is a very soft and very hydrophobic system. C3002-A is a very reactive crosslinker, which can work at temperatures as low as 80°C. C3003-A is a different type of cross-linkable aminosiloxane than C3001-A: it is less soft but rather hydrophilic. If it is not cross-linked with something like C3002-A, then the permanency is rather limited. C3009A is a self-crosslinkable Poly ethylenvinylacetate (EVA). It is not as hydrophilic as C3003-A but by far not as hydrophobic as C3001-A. This means that it can be made hydrophilic with suitable additives.

There are several reasons of the usage of coconut as one of the active ingredient inside of the capsules in this thesis:

- Together with coconut oil, a good microcapsule formation and dispersion can be obtained. Myritol 318 is a medium chain triglyceride prepared from fractionated coconut oil. Myritol 318 is clear, slightly yellowish, polar, odorless oil with a mean molecular weight. Due to its mean spreading value, the product can be universally applied in cosmetic and pharmaceutical skin care preparations and well-fatting emulsions and skin oils.

- The blend of Myritol 318 with vitamin E is a model blend in this thesis. Both are relatively easy to analyze after extraction. Both are used a tracer for analytical purposes.

- Coconut oil has longer shelf life than the other oils. Around two years it can resists to environmental conditions and high temperature. This is very important characteristic to have long-life microcapsules, which have long shelf life active ingredient inside [219].

- Myritol 318 coconut oil in this thesis was used as one of typical emollients for it´s good skin properties, a good dissolving capacity of other cosmetic ingredients such as Vitamin E, E-Acetate and so on. Since vitamin E was also used in this thesis, coconut oil made a good dissolving function on vitamin E used. Vitamin E and Myritol blend homogeneously in nearly any proportions.

- Coconut oil improves digestion and absorption of fat-soluble vitamins such as vitamin E, minerals (especially calcium and magnesium), and amino acids.

The reasons of the usage of vitamin E as second active ingredient inside of the capsules in this thesis are:

- One of the typical characteristics of Vitamin E is that it may also simply characterized by its chromatographic behavior. That's why vitamin E was used in this study to make a quantitative tracing for further processes under gaschromatogram.

- α-tocopherol (α-TP), vitamin E is a representative anti-oxidant that dissolves in oil.

- α-tocopherol is the most biological active form of Vitamin E (over 10 times more potent than tocopherol acetate) and is highly effective as an antioxidant and free radical scavenger (tocopherol acetate is mainly effective as an antioxidant to formulation, not to the skin).

- α-tocopherol slows down the aging process while protecting and moisturizing the skin. However, when incorporated into cosmetic formulations in its naked form, Vitamin E oxidizes and loses its original activity. Therefore, microencapsulation process is extremely needed. The microcapsule protects α-tocopherol from oxidation and maintains its original activity after incorporation into cosmetic formulations.

3.4. Microcapsule Size Determination

Different mean size microcapsules were produced in the laboratory [218] by using different stirring rates that are likely analyzed by other researchers [19,23,118] Coulter equipment were used to identify the mean size distribution of each produced microcapsule group. (Fig.3.2)

Fig. 3.2: Coulter Equipment; Microcapsules are Placed in This Holes for Size Measurement

In this thesis, the mean size distribution of three different microcapsules were measured under Coulter Equipment and the mean size distribution graphic of microcapsule A, microcapsule B and microcapsule C are indicated in Fig.3.3, Fig.3.4 and Fig.3.5.

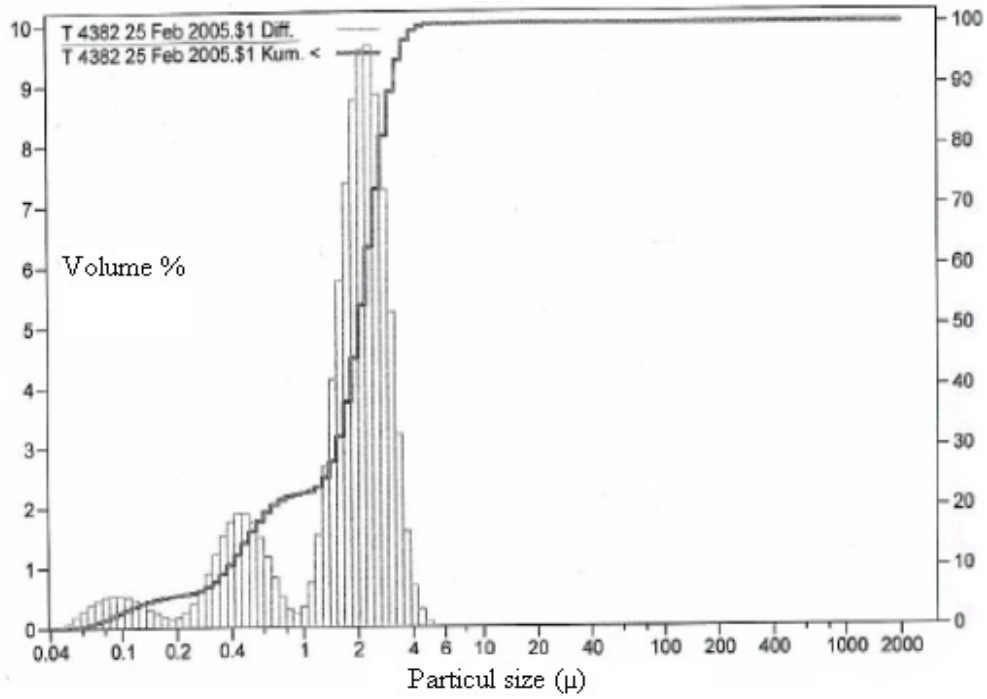


Fig. 3.3: Mean Size 1,938 µ. (Microcapsule A = > 2-3 µ)

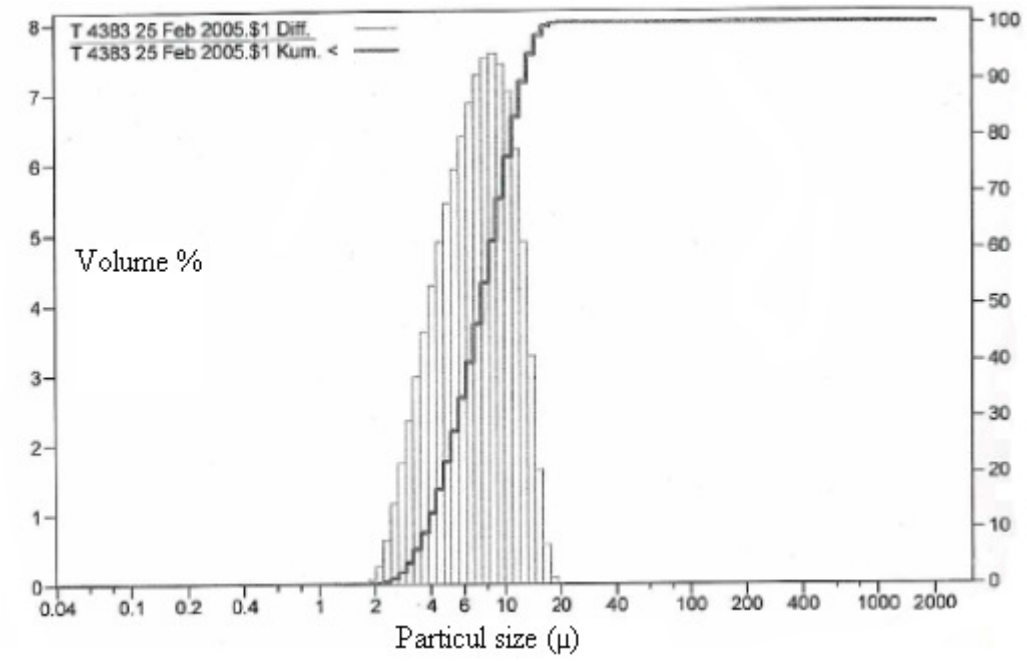


Fig. 3.4: Mean Size 7,077 µ. (Microcapsule B = > 8-10 µ)

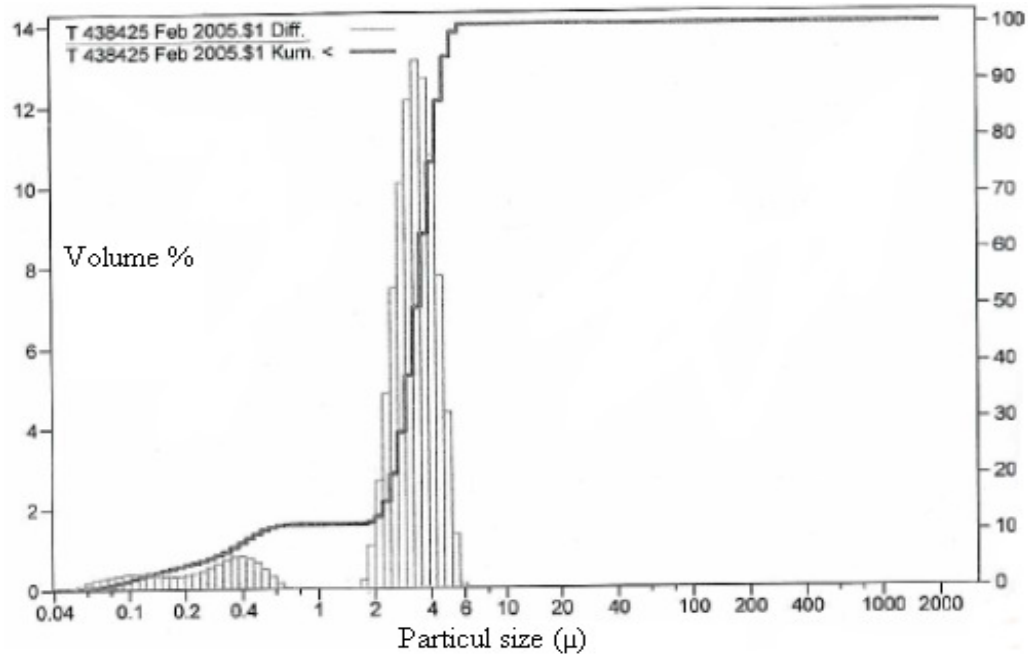


Fig. 3.5: Mean Size 3,208 µ. (Microcapsule C = > 3-4 µ)

3.5. Microcapsule Applications

In this thesis, two application processes were used for the microcapsule treatment on to the fabric:

- Exhaust method (Fig. 3.6) and
- Foulard method (Fig.3.7)

Fig. 3.6: Exhaust Method Equipment

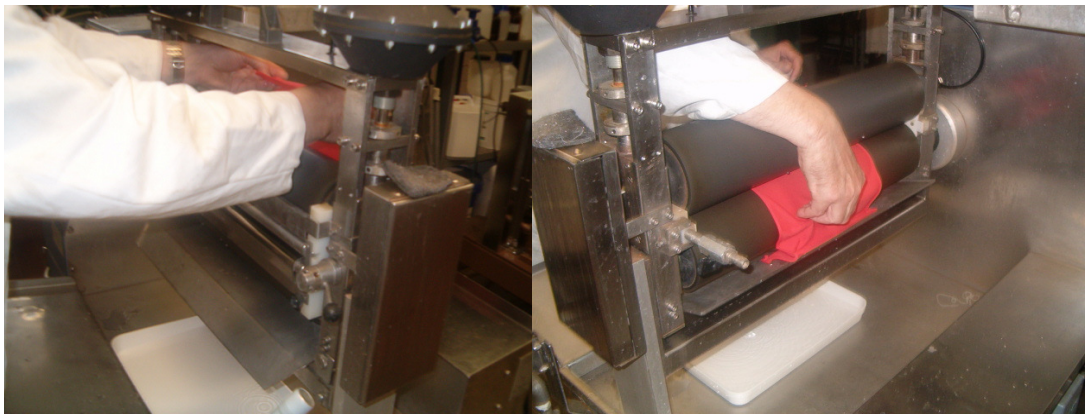


Fig. 3.7: Foulard Equipment

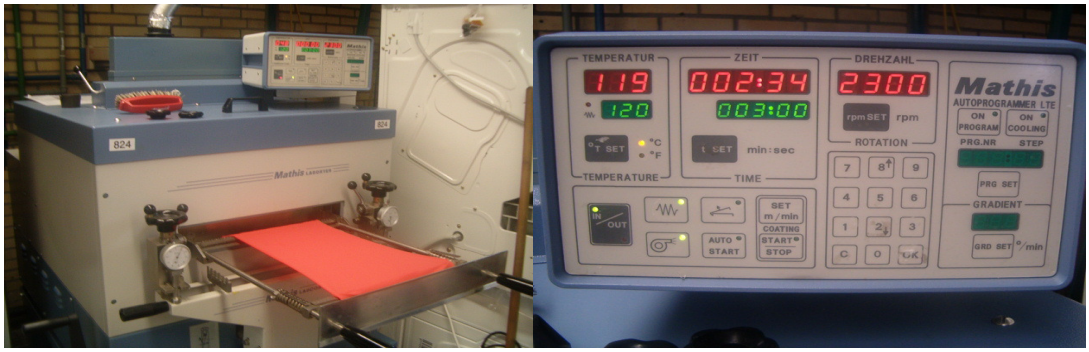


Fig. 3.8: Mathis Dryer

After the application of microcapsules on to the fabric, drying process followed by using Mathis Dryer (Fig.3.8).

3.5.1. Exhaust Method Recipes and Process Conditions

This is one of the two microcapsules application processes used in this thesis.

Capsule dispersion and fabric are placed in to the beaker and mixed together about 15 minutes at 40°C. At the initial stage of mixing process, pH is adjusted to between 4 - 4.5 by adding acetic acid (Fig 3.6).

After 15 minutes time, binder or binders are added and then additional 15 minutes mixing process is followed again at 40°C. Mixing process is obtained by using a magnetic fish in to the beaker. Mixing speed of magnetic fish is 250 rpm.

The last step is drying the fabric. Fabric is passed through the calendar cylinder and the water is squeezed. Squeezed fabric is dryed under 120 °C – 3 minutes in Mathis Dryer Machine. (Fig. 3.8)

The dry fabric is weighted within the closed bottle and compared with its initially dried weight before the application process. The fabric weight difference is the amount of the microcapsule and binder kept by the fabric.

Weight difference= Binder amount + Capsule on fabric after microcapsule treatment.

The liquor ratio used in exhaust process is 1:15 as seen in Table 3.2. 4 different exhaust application recipes were formed and applied on to fabric:

Table 3.2: Recipe1; Capsule B in Combination with Binder 3001A and 3002 A: Exhaust Method

Component	Percentage (related to textile)	Mass (g)
Water	1500%	218,85
Capsule Dispersion- FaSch 9024 - 016 B	10%	1,46
Binder 1- Dispersion - 3001A	8%	1,17
Binder 2- Dispersion (10%) - 3002A	0,33%	0,48
Total		221,96
Nanox 1166 (2g/lt)		0,44

Nanox 1166 is an aqueous solution of polyoxyethylene derivative. Nanox 1166 was provided from Cognis GmbH& Co. KG Laboratory, Germany. The reason of using this chemical is mainly to increase the microcapsule affinity to the fabric, which means, staying onto the fabric rather than staying in the liquor. In recipe 1 (Table

3.2), fabric swatch that is dried in Mathis Dry at 120 °C during 3 minutes is weighted as 14.59 g before recipe application.

The final dry fabric weight in recipe 1 is measured as 15.36 g after the application of recipe 1. So, the weight difference is calculated as:

14.59 g (fabric weight before application process) subtracts from 15.36 g (fabric weight after application process). Finally, 0.77 g is found out as the weight of microcapsule and binder remained on the fabric. (Table 3.2)

Table 3.3: Recipe 2; Capsule C in Combination with Binder 3001A and 3002 A: Exhaust Method

Component	Percentage (related to textile)	Mass (g)
Water	1500%	225,45
Capsule Dispersion - FaSch 9024 - 016 C	10%	1,503
Binder 1- Dispersion - 3001A	8%	1,2024
Binder 2- Dispsersion (10%)- 3002A	0,33%	0,496
Total		228,65
Nanox 1166 (2g/lt)		0,457

Fabric swatch weight before recipe 2 application was measured as 15.03 g. After the application, fabric was condensed at 120 °C during 3 minutes in Mathis Dryer Machine. The final dry fabric weight after the microcapsule treatment was measured as 16.19 g. So, the difference is calculated as 1.16 g. (Table 3.3)

Fabric swatch weight before recipe 3 application was measured as 15.21 g. After the application, fabric was condensed at 120 °C during 3 minutes in Mathis Dryer Machine. The final dry fabric weight after the microcapsule treatment was measured as 16.36 g. So, the difference is calculated as 1.15 g, which is binder and microcapsule weight. (Table 3.4)

Table 3.4: Recipe 3; Capsule A in Combination with Binder 3001A and 3002 A: Exhaust Method

Component	Percentage (related to textile)	Mass (g)
Water	1500%	228,15
Capsule Disp.- FaSch 9024 - 016 A	10%	1,521
Binder 1- Disp./Solution - 3001A	8%	1,217
Binder 2- Disp./Solution (10%)- 3002A	0,33%	0,50
Total		231,39
Nanox 1166 (2g/lt)		0,463

Table 3.5: Recipe 4; Without Nanox 1166: Exhaust Method

Component	Percentage (related to textile)	Mass (g)
Water	1500%	230,25
Capsule Dispersion - FaSch 9024 - 016 **A**	10%	1,54
Binder 1- Dispersion - 3001A	8%	1,228
Binder 2- Dispersion (10%)- 3002A	0,33%	0,51
Total		233,53

Fabric swatch weight before recipe 4 application was measured as 15.35 g. After the application, fabric was condensed at 120 °C during 3 minutes in Mathis Dryer Machine. The final dry fabric weight after the microcapsule treatment was measured as 16.33g. So, the difference is calculated as 0.98 g, which is binder and microcapsule weight. (Table 3.5)

3.5.2. Foulard Method Recipes and Process Conditions

This is the second microcapsule application processes used in this thesis. Laboratory type foulard was used in this method and the pick up percentage of the fabric is calculated:

Step **1**: The dry fabric weight is measured. (19,03g.)
Step **2**: Then fabric is padded with liquor water. Then fabric in wet condition is squeezed in foulard with the pressure of 5 bars and with the speed of 3m/min. The squeezed fabric weight is measured and found out as 29,40 g.

(29.40 – 19.03)/ 19.03 = 54.5%

54.5% is the pick up value for this fabric. Different type of recipe configurations were formed and applied on Supplex fabric quality by using different type of binder qualities and different size of microcapsule diameters as microcapsule A, microcapsule B and microcapsule C.

Nine different recipes were prepared (Table 3.6). And step by step:

1. Microcapsules, binder or binder combinations are added in to the beaker with the mentioned amounts in its recipe.

Table 3.6: "9" Different Foulard Recipes

Recipe 1		
To obtain on 5% 3001A	(5*100/54.4)	9.19 g
To obtain on 0.5% 3002A	(0.5*100/54.4)	0.92 g
To obtain on 7% Microcapsule **A**	(7*100/54.4)	12.87 g
Total weight of chemicals		22.98 g
H_2O		77.02 g
Grand Total		100 g

Recipe 2		
To obtain on 5% 3003A	(5*100/54.4)	9.19 g
To obtain on 7% Microcapsule **A**	(7*100/54.4)	12.87 g
Total weight of chemicals		22.06 g
H_2O		77.94 g
Grand Total		100 g

Recipe 3		
To obtain on 5% 3009A	(5*100/54.4)	9.19 g
To obtain on 7% Microcapsule **A**	(7*100/54.4)	12.87 g
Total weight of chemicals		22.06 g
H_2O		77.94 g
Grand Total		100 g

Recipe 4		
To obtain on 5% 3001A	(5*100/54.4)	9.19 g
To obtain on 0.5% 3002A	(0.5*100/54.4)	0.92 g
To obtain on 7% Microcapsule **B**	(7*100/54.4)	12.87 g
Total weight of chemicals		22.98 g
H_2O		77.02 g
Grand Total		100 g

Recipe 5		
To obtain on 5% 3003A	(5*100/54.4)	9.19 g
To obtain on 7% Microcapsule **B**	(7*100/54.4)	12.87 g
Total weight of chemicals		22.06 g
H_2O		77.94 g
Grand Total		100 g

Recipe 6		
To obtain on 5% 3009A	(5*100/54.4)	9.19 g
To obtain on 7% Microcapsule **B**	(7*100/54.4)	12.87 g
Total weight of chemicals		22.06 g
H_2O		77.94 g
Grand Total		100 g

Recipe 7		
To obtain on 5% 3001A	(5*100/54.4)	9.9 g
To obtain on 0.5% 3002A	(0.5*100/54.4)	0.92 g
To obtain on 7% Microcapsule **C**	(7*100/54.4)	12.87 g
Total weight of chemicals		22.98 g
H_2O		77.02 g
Grand Total		100 g

Recipe 8		
To obtain on 5% 3003A	(5*100/54.4)	9.19 g
To obtain on 7% Microcapsule **C**	(7*100/54.4)	12.87 g
Total weight of chemicals		22.06 g
H_2O		77.94 g
Grand Total		100 g

Recipe 9		
To obtain on 5% 3009A	(5*100/54.4)	9.19 g
To obtain on 7% Microcapsule **C**	(7*100/54.4)	12.87 g
Total weight of chemicals		22.06 g
H_2O		77.94 g
Grand Total		100 g

2. The fabric swatch is placed in to the bottle.

3. After fabric gets totally wet, then, it is taken out from the bottle and it is passed through the foulard cylinders with the pressure of 5 bars and with the speed of 3 m/min. (Fig. 3.7)

4. The squeezed fabric is placed in to the Mathis-Dryer for further drying process during 3 minutes at 120^0C. (Fig. 3.8)

In these 9 different recipes listed in Table 3.6, microcapsule size and the binder qualities are the important parameters that play active role in washing durability.

3.5.3. Chitosan Coating Recipes in Foulard and Process Conditions

Since the lost index rate in further gas-chromatographic analyses was better among the used binder qualities in C3001A+C3002A than that of the others in foulard process, which means the recipe 1, recipe 4 and recipe 7; just these three recipes were also chitosan coated for further comparison for the lost index rate improvement in foulard process. Already microcapsule treated fabric was passed through the second foulard bath that contains chitosan lactic acid solution. (Table 3.7)

Table 3.7: Chitosan Coating of Microcapsule Treated Fabric by Second Foulard Process

Recipe C1		
I. Foulard Process		
To obtain on 5% 3001A	(5*100/54.4)	9.19 g
To obtain on 0.5% 3002A	(0.5*100/54.4)	0.92 g
To obtain on 7% Microcapsule **A**	(7*100/54.4)	12.87 g
Total weight of chemicals		22.98 g
H_2O		77.02 g
Grand Total		100 g
II. Foulard Process		
Chitosan coating by second foulard process	3% Chitosan 1.6% lactic acid in foulard bath	Finally, 120°C 3 minutes drying

Recipe C4		
I. Foulard Process		
To obtain on 3001A	(5*100/54.4)	9.19 g
To obtain on 0.5% 3002A	(0.5*100/54.4)	0.92 g
To obtain on 7% Microcapsule **B**	(7*100/54.4)	12.87 g
Total weight of chemicals		22.98 g
H_2O		77.02 g
Grand Total		100 g
II. Foulard Process		
Chitosan coating by second foulard process	3% Chitosan 1.6% lactic acid in foulard bath	Finally, 120°C 3 minutes drying

Recipe C7		
I. Foulard Process		
To obtain on 3001A	(5*100/54.4)	9.9 g
To obtain on 0.5% 3002A	(0.5*100/54.4)	0.92 g
To obtain on 7% Microcapsule **C**	(7*100/54.4)	12.87 g
Total weight of chemicals		22.98 g
H_2O		77.02 g
Grand Total		100 g
II. Foulard Process		
Chitosan coating by second foulard process	3% Chitosan 1.6% lactic acid in foulard bath	Finally, 120°C 3 minutes drying

3.6. Washing Process

Fabric with different recipes applied via exhaust and foulard methods were washed as; one time, three times, five times, seven times, nine times and ten times in wascator. Washing process was made according to the BS EN ISO 6330:2001,8A, during 30 minutes at 30 °C as gentle cycle. Ece, type A, detergent that does not contain optical brightening was used. The machine load was 2.0 kg. The amount of the detergent was 40g and the amount of sodium perborat was 10g, respectively 4:1 ratio. Flat dry was made after each washing cycles to the fabric swatches.

3.7. Coating and SEM Analysis

A small fabric swatch (around 2 g.) were cut after each washing cycle after drying and the samples placed on to the plate for gold coating process in order to prepare to analysis via scanning electron- microscope (Fig.3.9).

Figure 3.9: Emitechi Coating Device; (a) Supplex Fabric Treated with Microcapsule were Coated with Gold in Vacuum Conditions; (b) Emitechi Coating Device; (c) After The Coating, The Coated Supplex Fabric Swatches.

The coated fabric swatches were examined under the scanning electron- microscope (Fig 3.10) and the photographs were taken.

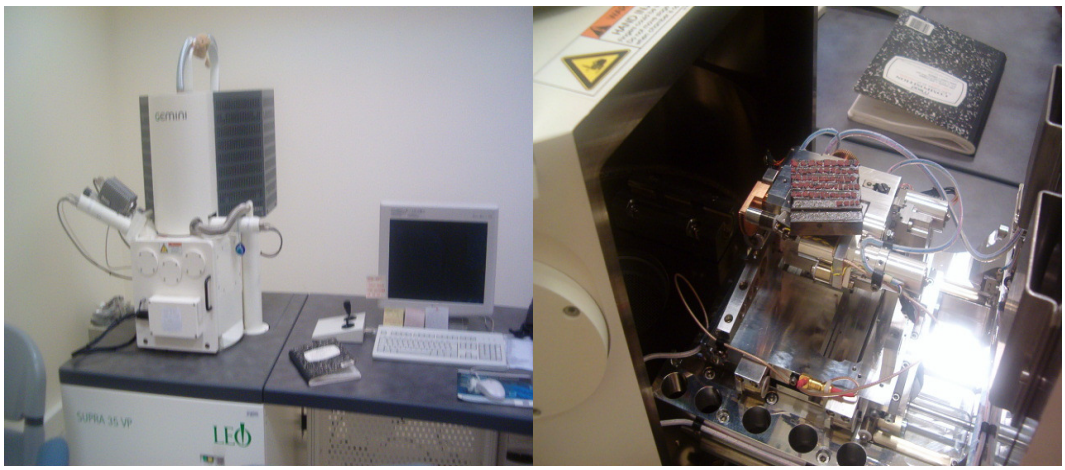


Fig. 3.10: Scanning Electron- Microscope (SEM) – LEO/ Gemini Supra 35 VP

3.8. Gas-chromatographic Analyses

Gas chromatographic analysis was made by Agilent 6890[323]. The fabric swatches microencapsulated by exhaust and foulard methods with different recipes and washing cycles were analyzed by gas chromatogram to measure the active ingredient amount on the fabric after each washing cycle. Moreover, the fabric swatches coated with chitosan were also tested by gas chromatogram to analyze the influence of chitosan coating on washing durability.

Gas chromatographic examination by mass spectrometric detection:

Gas chromatograph	:	Agilent 6890
Temperature programme	:	75 °C, 0.5 min.
Column	:	J&W DB-5HT
		30 m x 0.32 mm x 0.1 µm film
Carrier gas	:	helium, 2ml/ min
Detector	:	MS, Quad: 200 °C, source 250 °C,
		Scan 50-500 m/z
Injector	:	320 °C
Injection	:	2 µl split 20:1
Sample preparation	:	A liquids of the samples are treated with

tetrahydrofuran containing the internal standard (tetradecane) and placed in an ultrasonic bath for 30 min at 70 °C. The extract is analyzed by gas chromatography. The evaluation is done by the internal standard method [220]. Myritol 318 was used as reference substance (AU064844) from Cognis GmbH.

4. RESULTS AND DISCUSSION

4.1. Laundering Durability Evaluation of Exhausts Recipes

In SEM images (Fig 4.3 – Fig 4.6), it is seen that the shape of produced microcapsules in this thesis are spherical. The core content and encapsulation efficiency are confirmed by gas-chromatographic analyses.

The evaluation of the laundering durability for exhaust recipes were made in consideration with

- The image analyses by visual obtained by scanning electron-microscopy (Fig 4.3 - Fig 4.6).
- The quantitative amount analyses of vitamin E and myritol 318 coconut oil by gas-chromatogram. (Table 4.1, Table 4.2 and Fig 4.1 and Fig. 4.2)

Table 4.1: Gas-chromatographic Analysis of Vitamin E in Microencapsulated Fabric by Exhaust Method

Recipe Type	Average Vitamin E weight % (w/w)	Release Amount By Weight %	Lost Index
Recipe 1 with capsule B - before wash	0,136		1,000
Recipe 1 with capsule B - 10 wash	0,121	0,015	**0,890**
Recipe 2 with capsule C - before wash	0,146		1,000
Recipe 2 with capsule C - 10 wash	0,114	0,032	**0,781**
Recipe 3 with capsule A - before wash	0,144		1,000
Recipe 3 with capsule A - 10 wash	0,098	0,046	**0,681**
Recipe 4 with capsule A - before wash	0,139		1,000
Recipe 4 with capsule A - 10 wash	0,098	0,041	**0,705**

Table 4.2: Gas-chromatographic Analysis of Myritol 318 Coconut Oil in Microencapsulated Fabric by Exhaust Method

Recipe Type	Average Myritol 318 coconut oil weight % (w/w)	Release Amount By Weight %	Lost Index
Recipe 1 with capsule B - before wash	2,550		1,000
Recipe 1 with capsule B - 10 wash	1,950	0,60	**0,765**
Recipe 2 with capsule C - before wash	2,270		1,000
Recipe 2 with capsule C - 10 wash	1,590	0,68	**0,700**
Recipe 3 with capsule A - before wash	2,370		1,000
Recipe 3 with capsule A - 10 wash	1,220	1,15	**0,515**
Recipe 4 with capsule A - before wash	2,150		1,000
Recipe 4 with capsule A - 10 wash	1,280	0,87	**0,595**

Lost index is calculated by dividing the capsule's vitamin E and myritol 318 amounts after 10 wash cycles to their initial amount before washing. Since the binder combination 3001A and crosslinking agent 3002A were the most sutiable ones for exhaust method, the other binder qualities were not used, because they were not suitable for exhaustion.

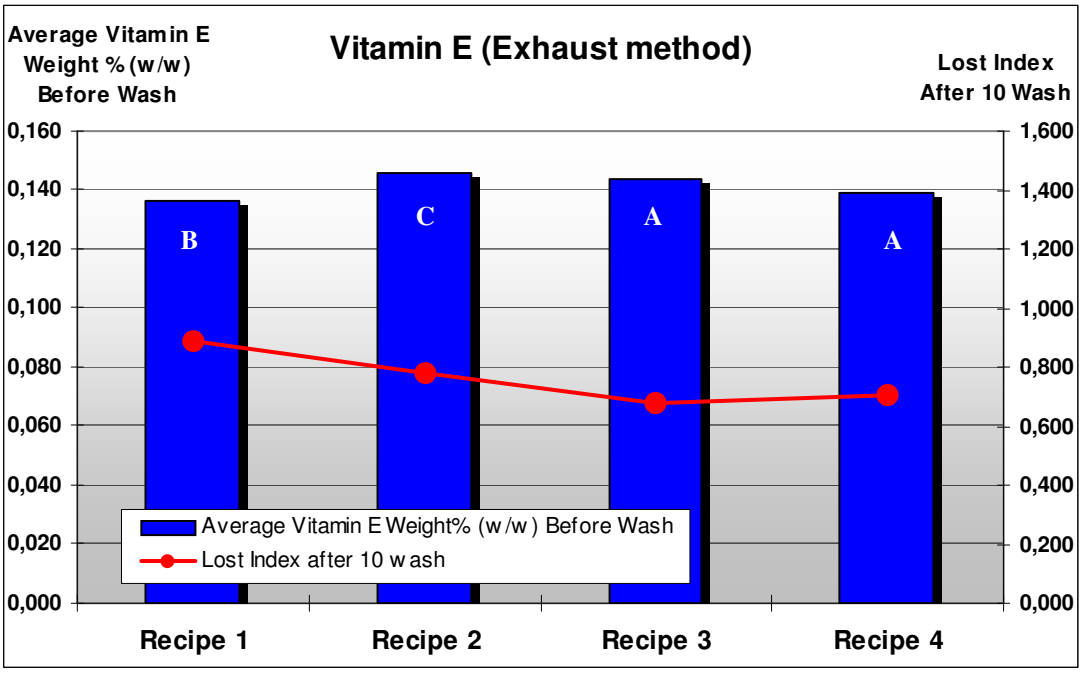


Fig. 4.1: Gas-chromatographic Analyses of Vitamin E in Microencapsulated Fabric by Exhaust

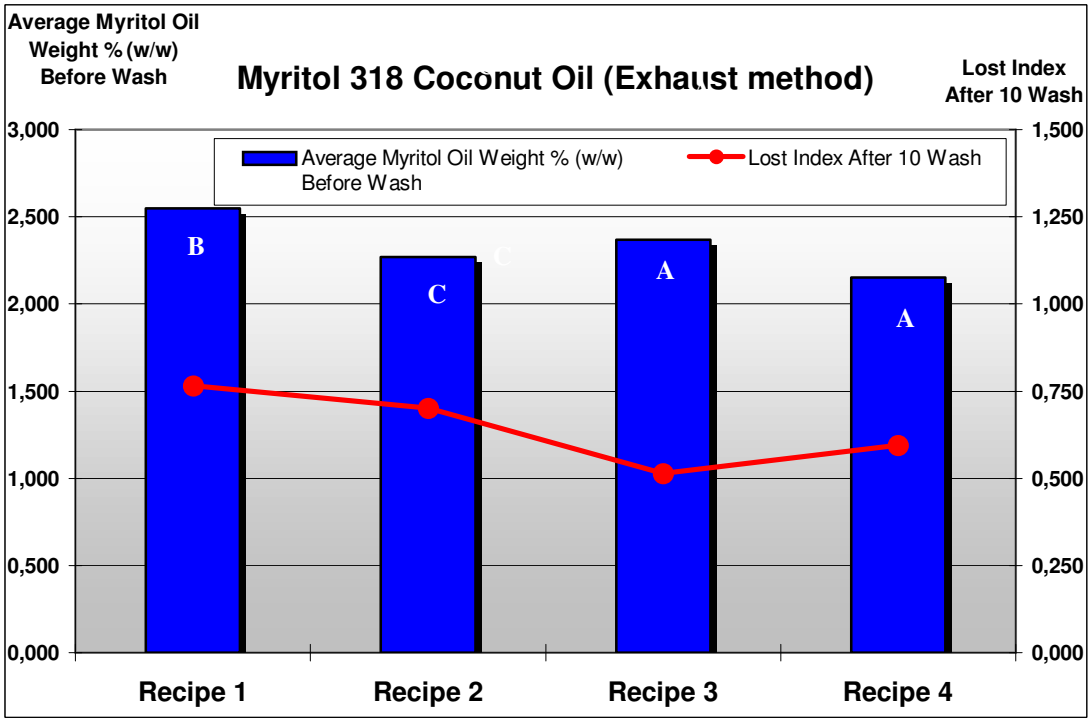


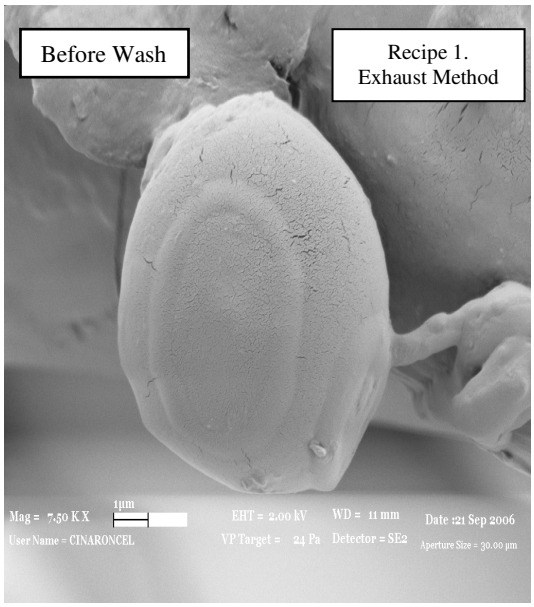
Fig. 4.2: Gas-chromatographic Analysis of Myritol 318 Coconut Oil in Microencapsulated Fabric by Exhaust

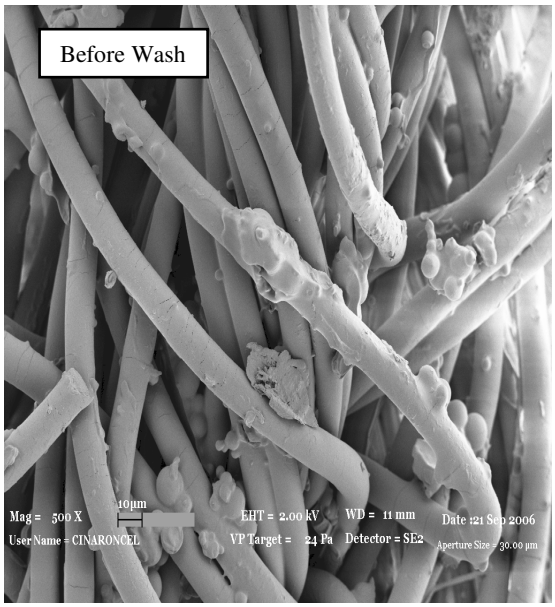
In comparison of each 4 recipes to each other in exhaust method, it can be concluded that the laundering durability performance of both capsule B and capsule C, which means bigger size capsules, were much better than that of capsule A, which is the smallest capsule size used in this thesis. This can be clearly seen in both vitamin E and myritol 318 coconut oil gas-chromatogram results in Fig. 4.1 and Fig. 4.2. As also pointed by Yamamoto et al. [95,121], the reason behind of this result should be that smaller particle size microcapsules would have larger total specific surface area, therefore causes its release rate to be faster than that of larger particle size microcapsules. It was also pointed out that the oil release rate increases when the diameter of microcapsules decreases by Wen-Chuan H, Chih-Pong C, Ying-Lin G in 2006 [118]. The bigger the capsule diameter means the thicker the capsule shell. This affected the release rate as well and the thicker capsule membrane helped to get slower release rate and minimize the risk of the capsule shell breakage.

However, the difference between the lost index of capsule A, B and C is not that much like in foulard process due to usage of same binder combination (3001A+3002A) in all recipes, it varies between 0,595 weight % (w/w) to 0,89 weight % (w/w).

The reason of using Nanox 1166 chemical was mainly to increase the microcapsule affinity to the fabric, which means, staying onto the fabric rather than staying into the liquor bath. In Fig. 4.6, Nanox 1166 was not used on purpose to examine this situation under scanning-electron microscope. Recipe 3 and recipe 4 is totally same, except; in recipe 3, Nanox 1166 was used and in the recipe 4 was not. As can be seen in Fig 4.1 and Fig 4.2, due to the increment of the affinity by Nanox 1166, the initial amount of vitamin E and myritol 318 coconut oil before washing are higher, but after 10 washing cycle there isn't much advantages of Nanox 1166.

When Fig 4.1 and Fig 4.2 compared with each other, it is seen that the release amounts of both vitamin E and myritol 318 coconut oil is quite similar. These results are confirming the correction of gas chromatographic analyses measurements. The decrease on both myritol 318 coconut oil and vitamin E is mainly because of the friction and the environmental conditions that fabric exposed. The active ingredient decrease happens either with the capsule burst or with a total capsule loss from fabric surface.


Before Wash
Recipe 1.
Exhaust Method
Mag = 7.50 K X
1µm
EHT = 2.00 kV
WD = 11 mm
Date :21 Sep 2006
User Name = CINARONCEL
VP Target = 24 Pa
Detector = SE2
Aperture Size = 30.00 µm


Before Wash
Mag = 500 X
10µm
EHT = 2.00 kV
WD = 11 mm
Date :21 Sep 2006
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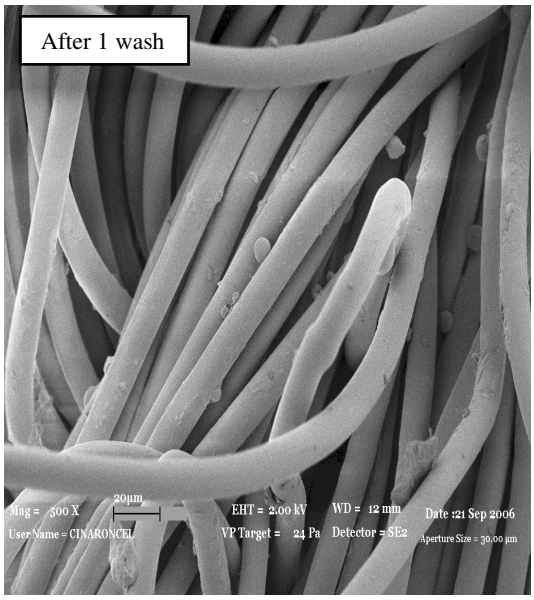
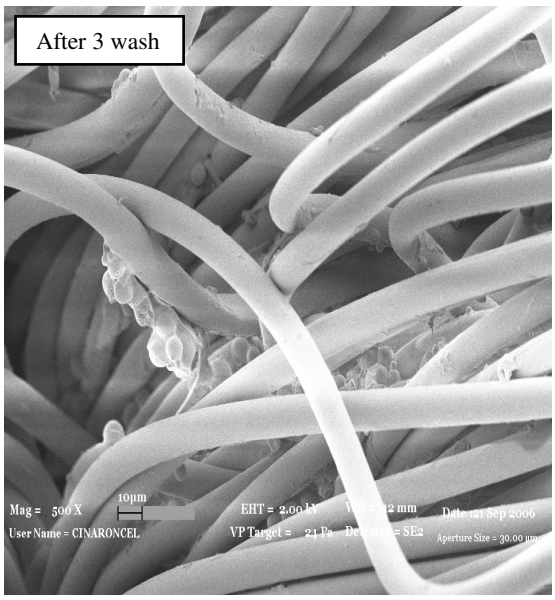
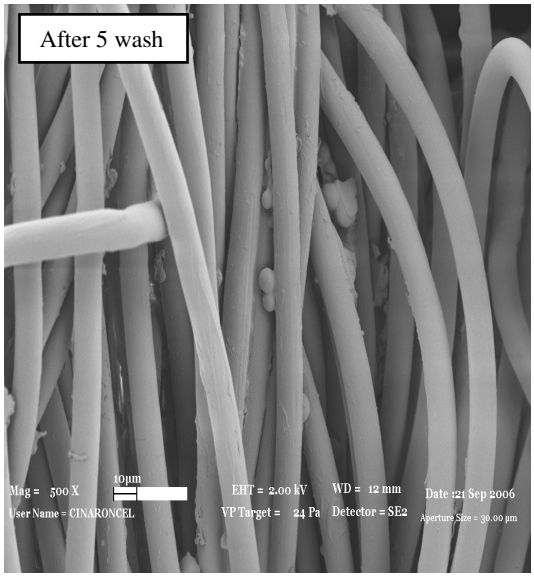
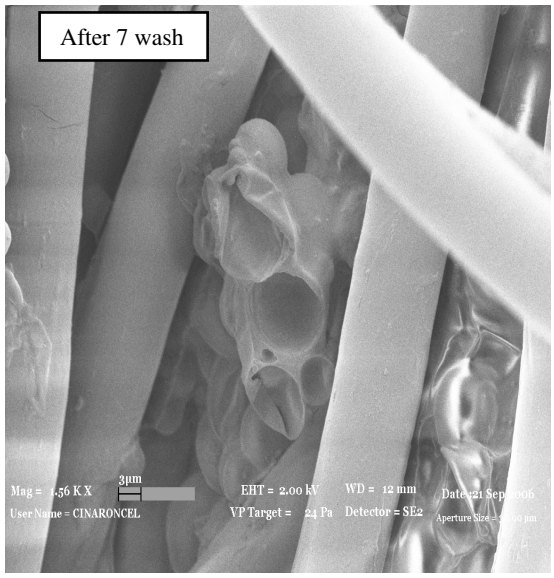
VP Target = 24 Pa
Detector = SE2
Aperture Size = 30.00 µm


After 1 wash
Mag = 500 X
20µm
EHT = 2.00 kV
WD = 12 mm
Date :21 Sep 2006
User Name = CINARONCEL
VP Target = 24 Pa
Detector = SE2
Aperture Size = 30.00 µm


After 3 wash
Mag = 500 X
10µm
User Name = CINARONCEL
VP Target = 24 Pa


After 5 wash
Mag = 500 X
10µm
EHT = 2.00 kV
WD = 12 mm
Date :21 Sep 2006
User Name = CINARONCEL
VP Target = 24 Pa
Detector = SE2
Aperture Size = 30.00 µm


After 7 wash
Mag = 1.56 K X
3µm
EHT = 2.00 kV
WD = 12 mm
User Name = CINARONCEL
VP Target = 24 Pa
Detector = SE2

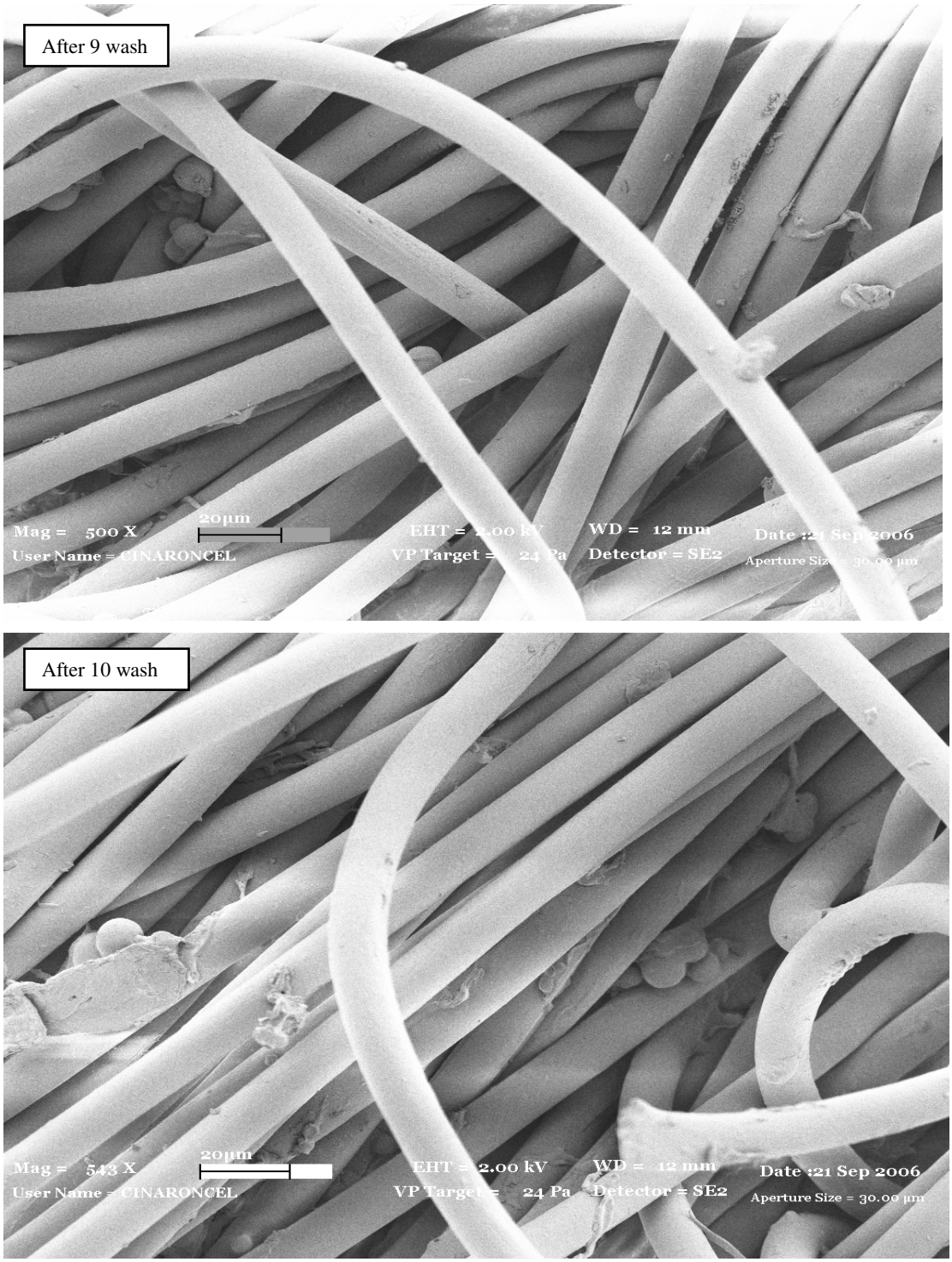
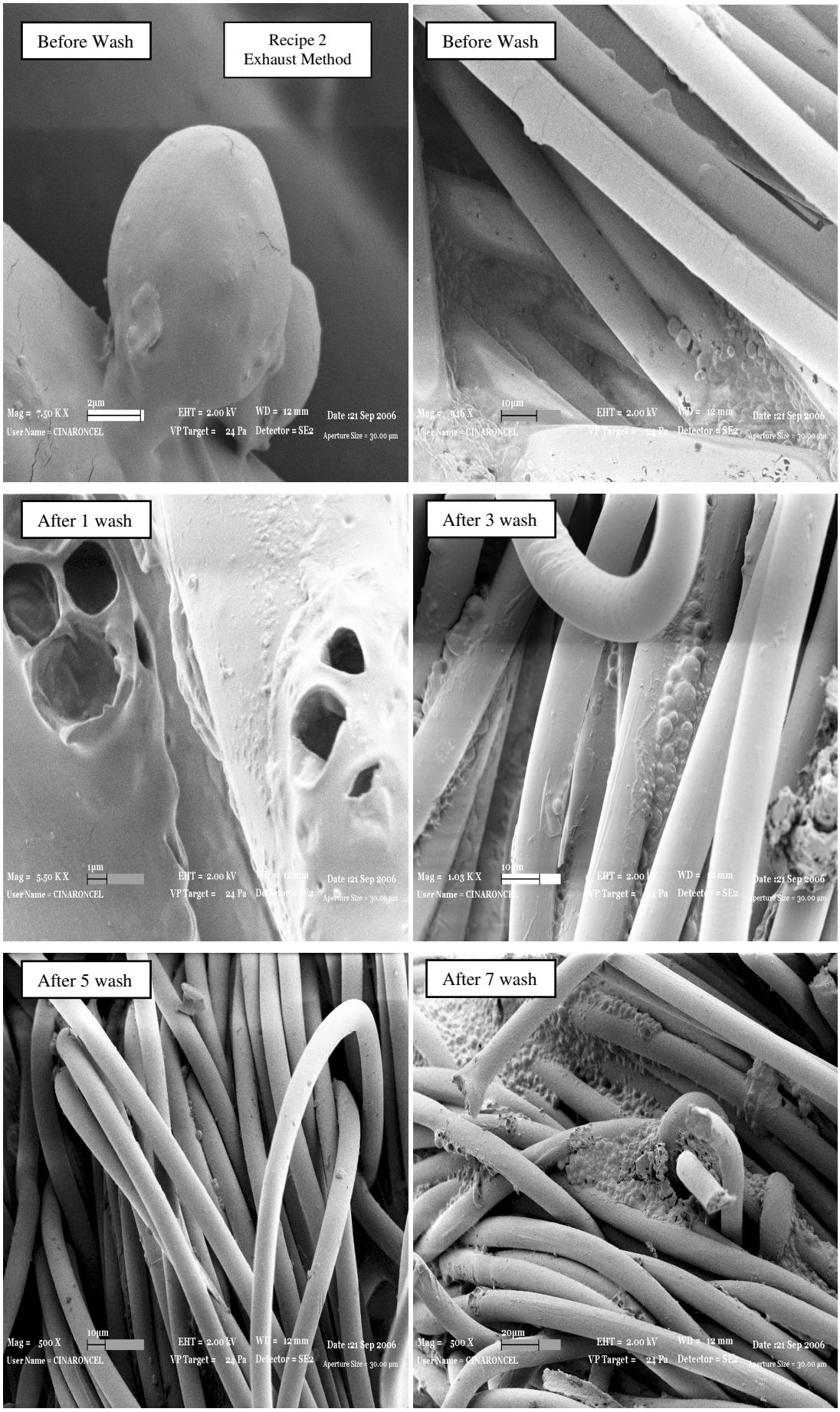


Fig. 4.3: Recipe 1. Exhaust Method

Figure 4.3 shows the image photos of the samples applied with exhaust method Recipe 1. It is seen that in the top figure, the magnified shape of microcapsule. It is spherical and it is bounded strictly to the fiber. After seven washes, it seems that some of the capsules are damaged or bursted, but after 10 washing cycle there are still high amount of microcapsules on the yarn.


Before Wash
Recipe 2
Exhaust Method
Mag = 7.50 K X
2µm
EHT = 2.00 kV
WD = 12 mm
VP Target = 24 Pa
Detector = SE2
Date :21 Sep 2006
Aperture Size = 30.00 µm
User Name = CINARONCEL
Before Wash
10µm
After 1 wash
1µm
Mag = 5.50 K X
After 3 wash
Mag = 1.03 K X
After 5 wash
Mag = 500 X
After 7 wash
20µm

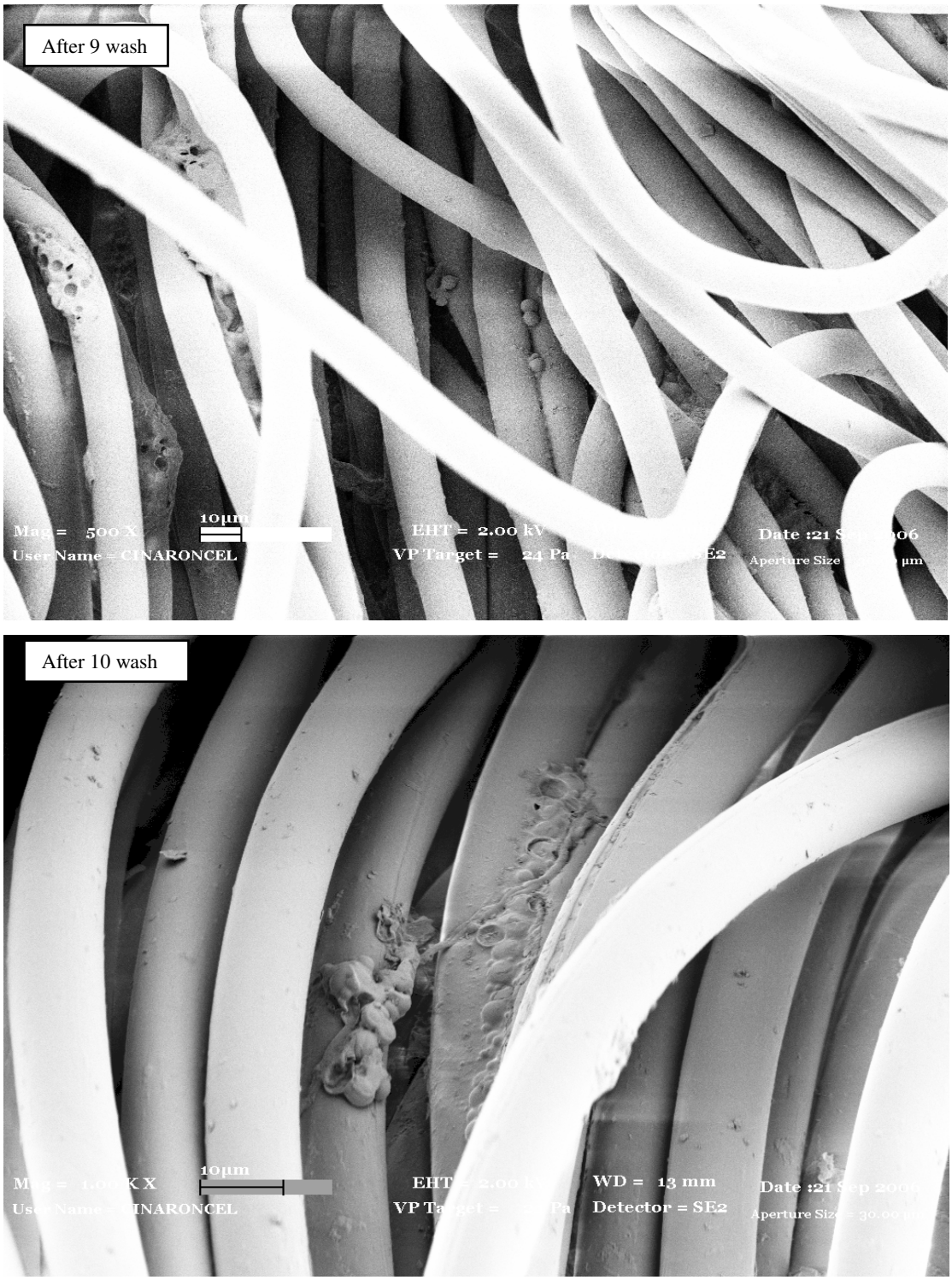
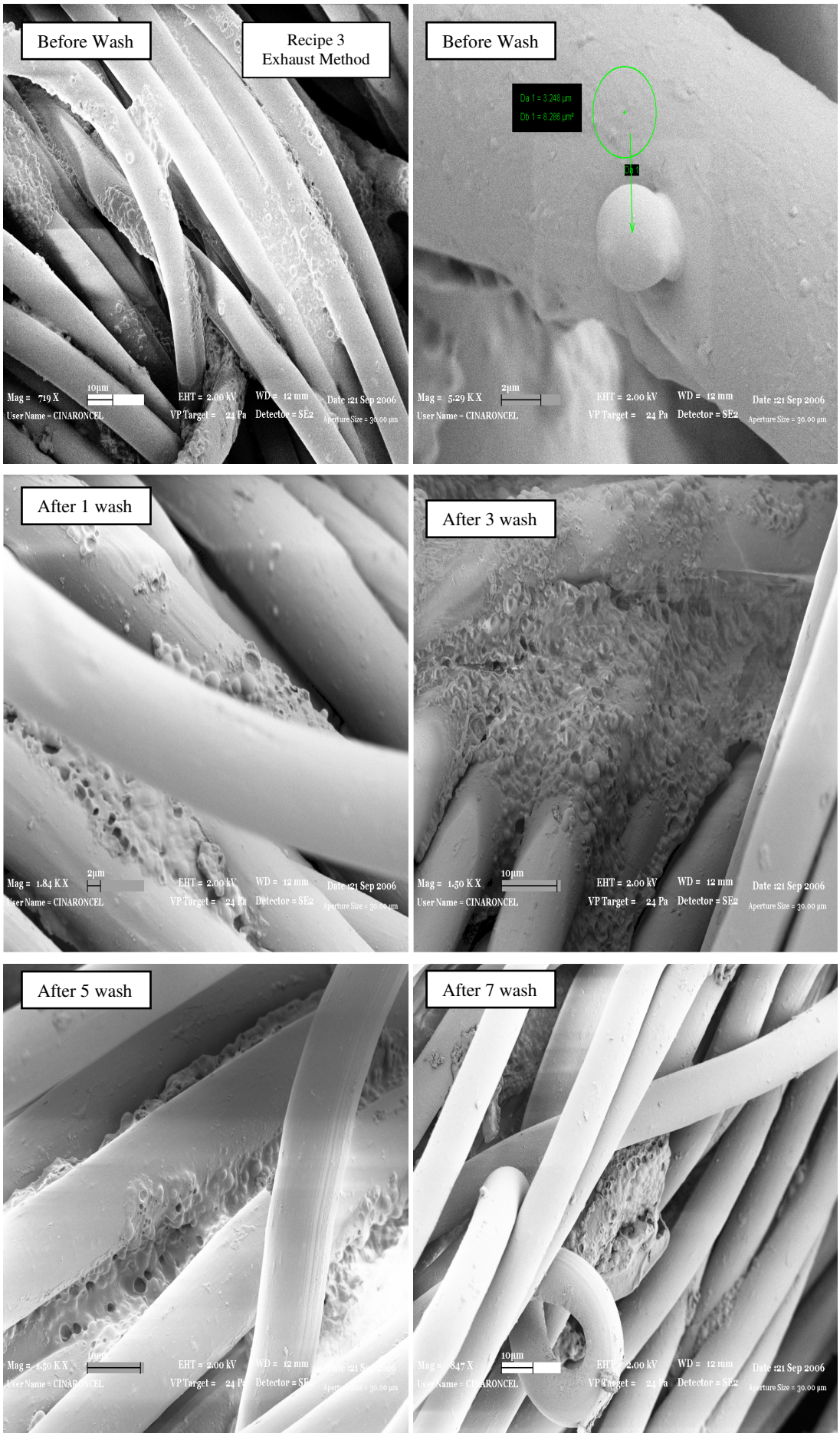


Fig. 4.4: Recipe 2. Exhaust Method

Figure 4.4 shows the fabric applied with Recipe 2. After 1 wash, clear bursting of the capsules is observed by SEM. After 7 washes, there are many capsules that attached to the yarn and to each other. It is also seen that there are microcapsules on the fabric after 10 washes.


Before Wash
Recipe 3
Exhaust Method
Mag = 719 X
10µm
EHT = 2.00 kV
WD = 12 mm
Date :21 Sep 2006
User Name = CINARONCEL
VP Target = 24 Pa
Detector = SE2
Aperture Size = 30.00 µm
Before Wash
Dia 1 = 3.248 µm
Db 1 = 8.286 µm²
Mag = 5.29 K X
2µm
EHT = 2.00 kV
WD = 12 mm
Date :21 Sep 2006
User Name = CINARONCEL
VP Target = 24 Pa
Detector = SE2
Aperture Size = 30.00 µm
After 1 wash
Mag = 1.84 K X
2µm
EHT = 2.00 kV
WD = 12 mm
Date :21 Sep 2006
User Name = CINARONCEL
VP Target = 24 Pa
Detector = SE2
Aperture Size = 30.00 µm
After 3 wash
Mag = 1.50 K X
10µm
EHT = 2.00 kV
WD = 12 mm
Date :21 Sep 2006
User Name = CINARONCEL
VP Target = 24 Pa
Detector = SE2
Aperture Size = 30.00 µm
After 5 wash
After 7 wash
10µm
EHT = 2.00 kV
WD = 12 mm
Date :21 Sep 2006
VP Target = 24 Pa
Detector = SE2
Aperture Size = 30.00 µm

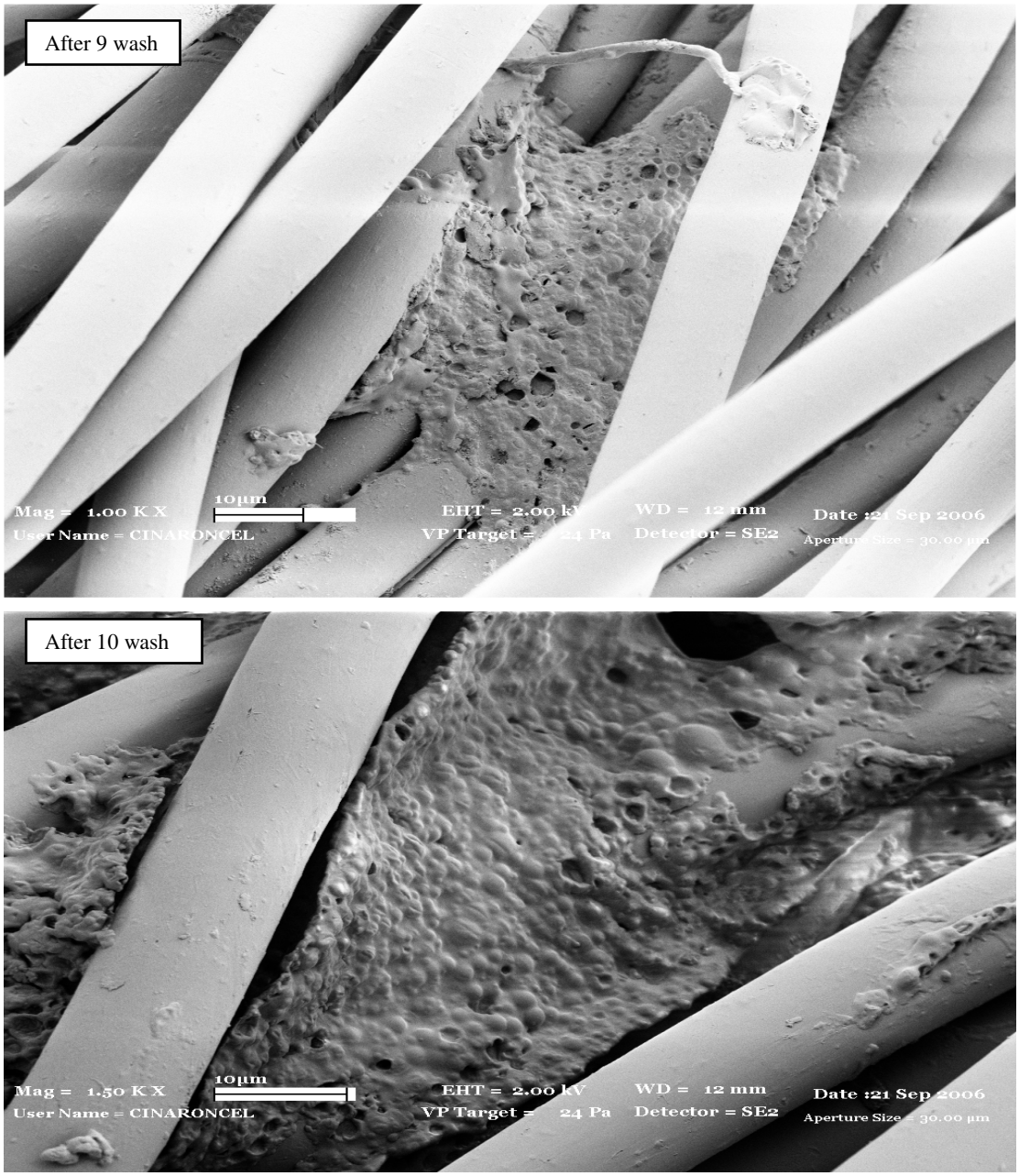
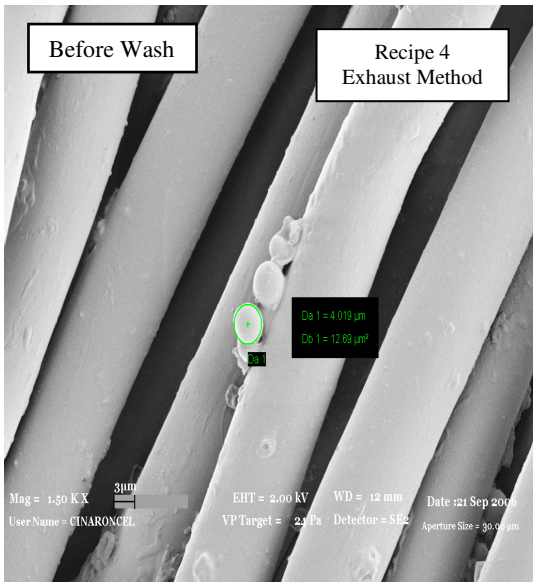
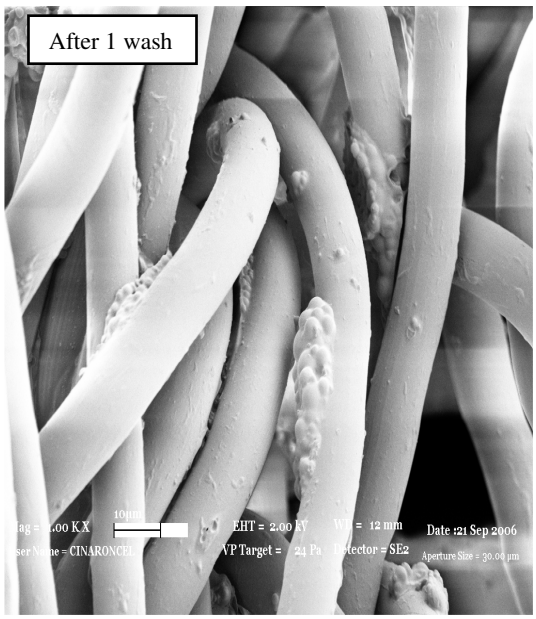


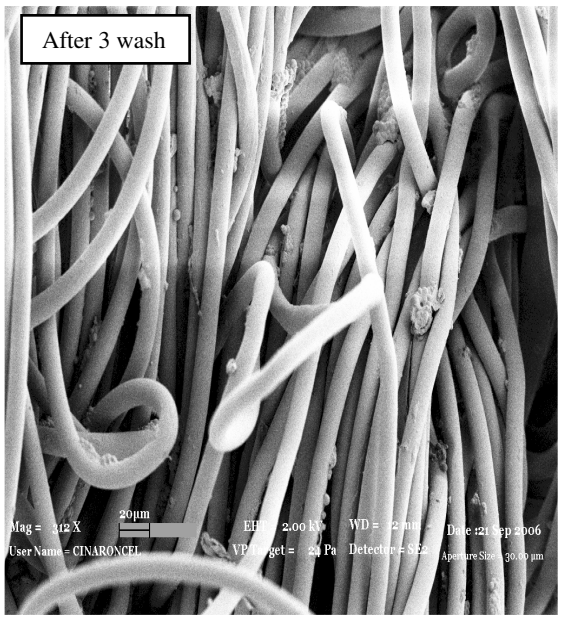
Fig. 4.5: Recipe 3. Exhaust Method

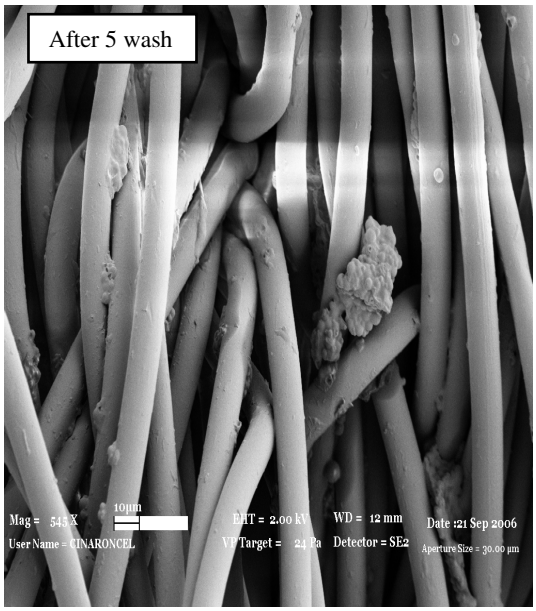
Figure 4.5 shows the fabrics applied with Recipe 3. After 1 wash, it is clearly seen that some of the capsules are already burst. After 10 wash most of the microcapsules are still bounded on yarn. On the other hand, most of the capsules are formed group together closely with each other and are not spread out homogenously.

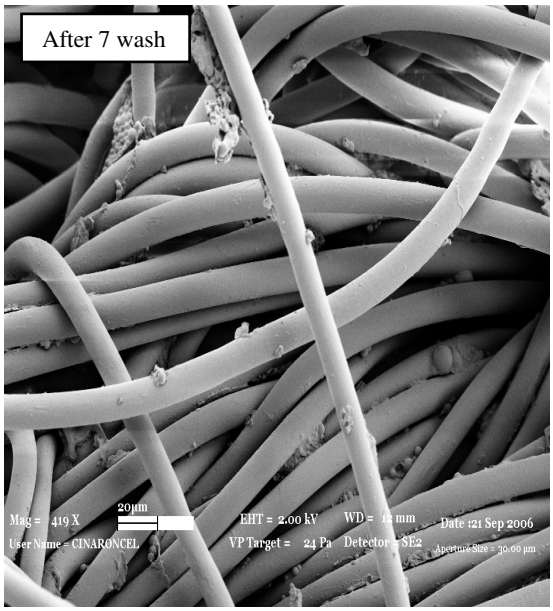

Before Wash
Recipe 4
Exhaust Method
Da 1 = 4.019 µm
Db 1 = 12.69 µm²
Da 1
Mag = 1.50 K X
3µm
EHT = 2.00 kV
WD = 12 mm
Date :21 Sep 2006
User Name = CINARONCEL
VP Target = 24 Pa
Detector = SE2
Aperture Size = 30.00 µm


Before Wash
Mag = 1.00 K X
10µm
EHT = 2.00 kV
WD = 12 mm
Date :21 Sep 2006
User Name = CINARONCEL
VP Target = 24 Pa
Detector = SE2


After 1 wash
10µm
EHT = 2.00 kV
Date :21 Sep 2006
VP Target = 24 Pa
Aperture Size = 30.00 µm


After 3 wash
Mag = 3.12 X
20µm
User Name = CINARONCEL


After 5 wash
Mag = 5.43 X
10µm
EHT = 2.00 kV
WD = 12 mm
Date :21 Sep 2006
User Name = CINARONCEL
VP Target = 24 Pa
Detector = SE2
Aperture Size = 30.00 µm


After 7 wash
Mag = 4.19 X
20µm
EHT = 2.00 kV
Date :21 Sep 2006
User Name = CINARONCEL
VP Target = 24 Pa
Detector = SE2

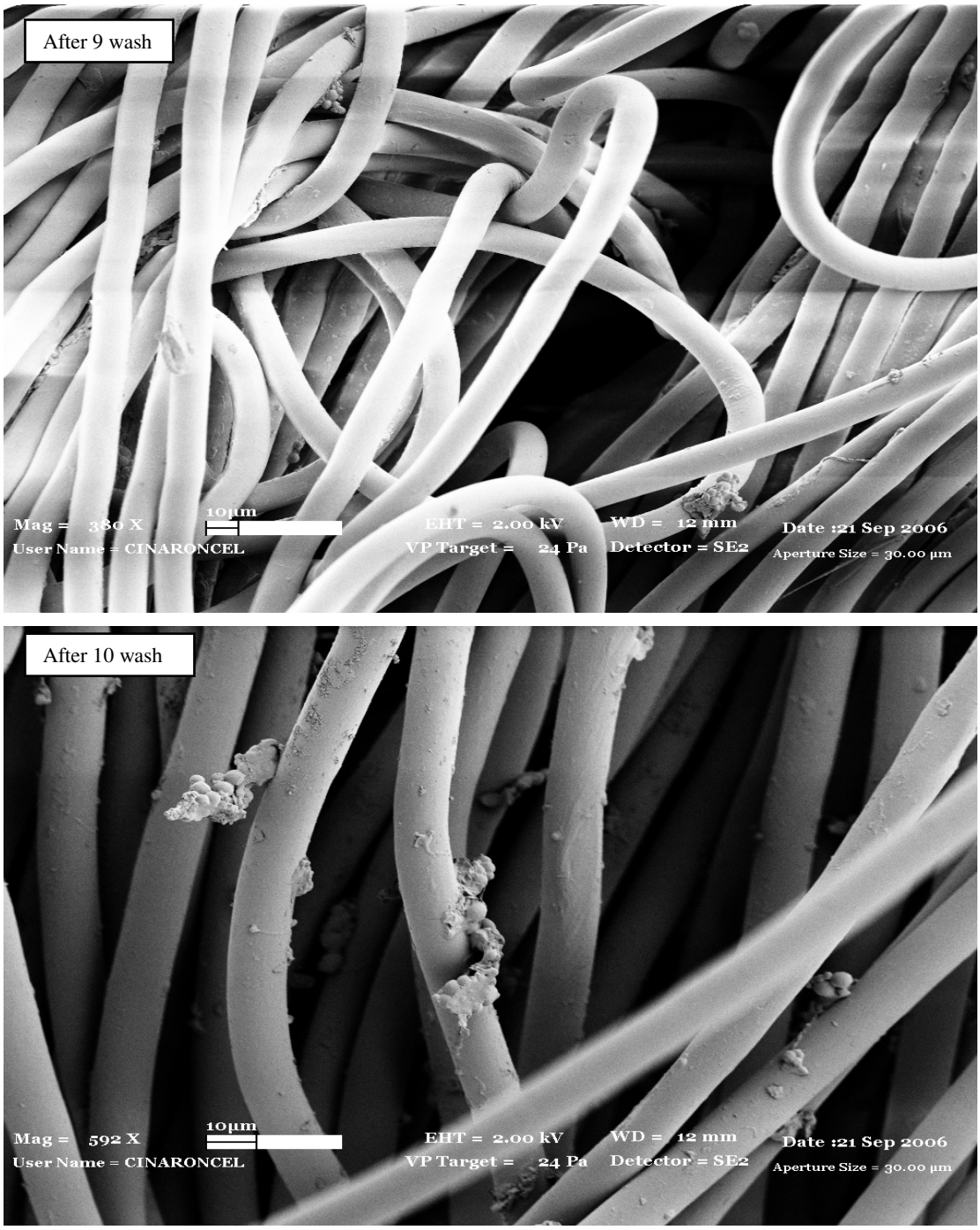


Fig. 4.6: Recipe 4. Exhaust Method

Figure 4.6 shows the fabrics applied with Recipe 4. In this recipe, capsules also formed groups in each washing cycle, but not that much bigger group like in Recipe 4.5. However, it is still seen that there are capsules after 10 wash cycles, but the amount of the capsules are not that much in high amounts like in Fig 4.3 and Fig 4.4.

4.2. Laundering durability evaluation of foulard recipes

The evaluation of the laundering durability for foulard recipes were made in consideration with

- The image analyses obtained by scanning electron-microscopy (Fig 4.12 - Fig 4.20).
- The quantitative amount analyses of vitamin E and myritol 318 coconut oil by gas-chromatogram. (Table 4.3, Table 4.4 and Fig 4.7 and Fig 4.8).

Table 4.3: Gas-chromatographic Analysis of Vitamin E in Microencapsulated Fabric by Foulard

Recipe type	Vitamin E Average% by weight - Before Wash	Average % Amount After 10 Wash	Release Amount By Weight %	Lost index After 10 Wash
Recipe I with capsule A	0,127	0,073	0054	0,575
Recipe 2 with capsule A	0,152	0,035	0,117	0,230
Recipe 3 with capsule A	0,129	0,100	**0,029**	**0,775**
Recipe 4 with capsule B	0,196	0,092	0,104	0,469
Recipe 5 with capsule B	0,042	0,019	0,023	0,452
Recipe 7 with capsule C	0,200	0,146	**0,054**	**0,730**

Table 4.4: Gas-chromatographic Analysis of Myritol 318 Coconut Oil in Microencapsulated Fabric by Foulard

Recipe type	Myritol 318 Average % by weight - Before wash	Average % Amount After 10 wash	Release Amount By Weight %	Lost index After 10 Wash
Recipe I with capsule A	1,290	0,727	0,563	0,564
Recipe 2 with capsule A	1,800	0,338	1,462	0,188
Recipe 3 with capsule A	1,260	0,939	**0,321**	**0,745**
Recipe 4 with capsule B	1,700	0,715	0,985	0,421
Recipe 5 with capsule B	0,261	0,094	0,167	0,360
Recipe 7 with capsule C	1,640	1,110	**0,530**	**0,677**

Binder comparison: Lost index of recipe 1 and recipe 3 are better than recipe 2 when same capsule size, capsule A was used in these three recipes. Because, the binder used in recipe 2 is not a strong binder like 3001A+3002A combination or 3009A. But, 3003A is not a very strong binder and is not resistant enough to wet processes. The poor performance of 3003A was also indicated itself in comparison with recipe 4 and recipe 5. Although capsule B used in both recipes, since 3003A was used in recipe 5, the release rate was quicker than that of recipe 4. Therefore, it is found that the worst performer binder quality is 3003A. This can be easily seen in Fig 4.7 and Fig 4.8. The average amount before wash is very low for Recipe 5, and

after 10 washes both Recipe 2 and Recipe 5 with the same binders have very low results in further home laundering cycles.

Binders should take the microcapsules release tendency under control. This can be provided by a good strong binder, which has hydrophobic properties. First off all, the binder has to have a strong adhesive characteristic and has to be enough resistant against water to protect the microcapsules.

Therefore, the best binders that have longer washing durability are (3001A+3002A) combination and 3009A. 3002A role is to harden and strengthen the surface of the microcapsules.

In our study, it was figured out that when examining the mean size of the microcapsules, microcapsules individually might behave differently than when they attach to the fabric by binders. It means, it is clear that smaller size of microcapsules will individually tend to release its active ingredient quicker than the bigger capsules, because, the diffusion rate and the risk of the capsule shell breakage will be higher in small size of capsules due to its thinner membrane wall. However, when the capsules are attached to the fabric, capsules behavior may be partly different due to the fact that the environment conditions of the capsule are different than its individual statement. Binder makes this difference. Normally, smaller size of capsules diffusion rate is higher due to its bigger surface than bigger capsules in the same weight proportion. However, the coverage of the binder also helps to improve the release rate for smaller size capsules and their breaking risk gets lowered like the big size of capsules. On the other hand, it is not requested that microcapsules totally sink under the binders. Otherwise, their active ingredient is totally dead and could not perform anymore. In this point, the best controllable release rate is needed. In this thesis, it is seen that for the bigger size of capsules, the lost index was much better in exhaust method. But, for small size of capsules (capsule A), due to the better binder coverage than that of the bigger capsule, capsule B, it gave us better release performance, than capsule B in foulard process as seen in Fig 4.7. (Except binder 3003 A - recipe 2, it is already the worse performer recipe due to the binder characteristic). In this thesis, the gas chromatographic analyses for by foulard process in Recipe 6, 8 and 9 were not made and just visual analyses by SEM analyses of them were examined in Fig. 4.17, 4.19 and 4.20. It is seen that release amounts are similar for vitamin E and Myritol 318 coconut oil after 10 wash cycles in Fig 4.8 and 4.9.

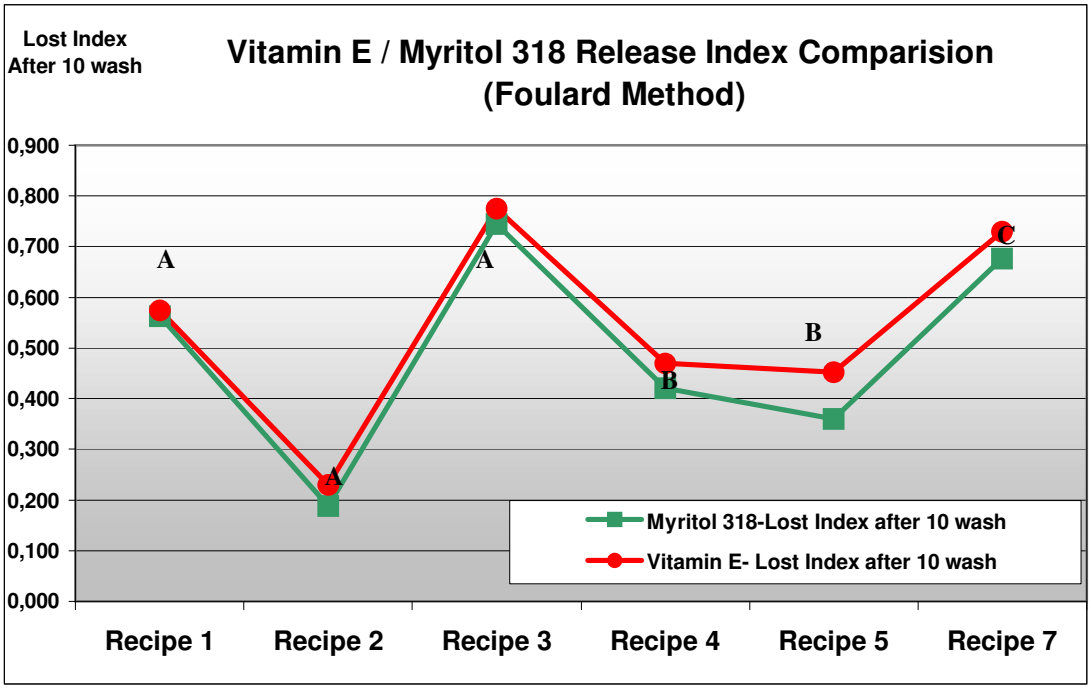


Fig 4.7: Lost index Comparison of Vitamin E and Myritol 318 Coconut Oil in Foulard Method

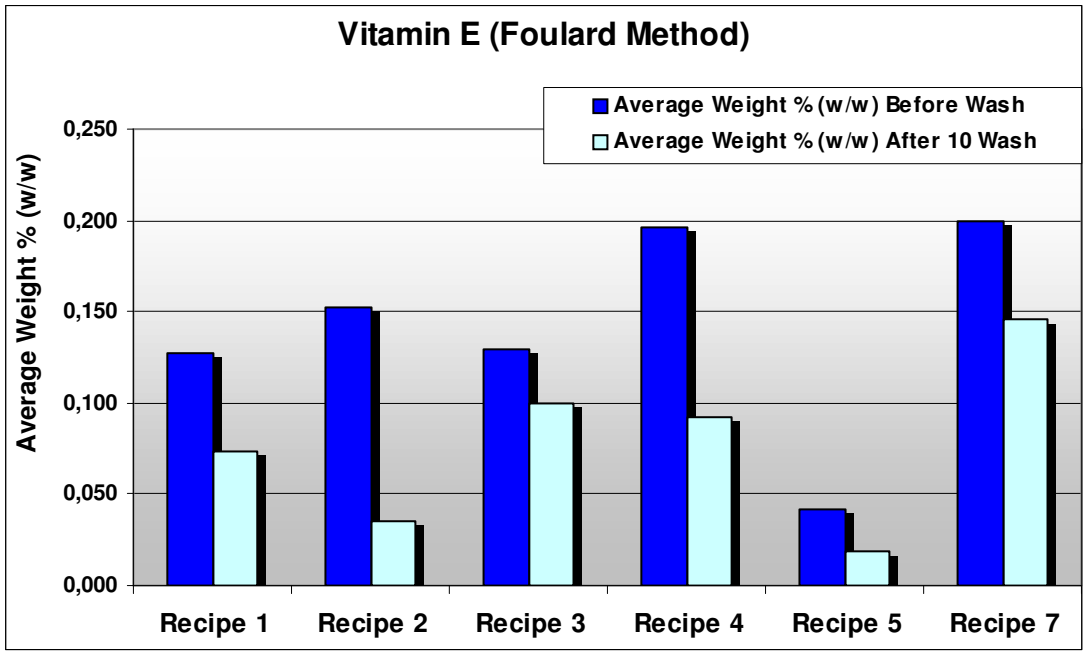


Fig. 4.8: Gas-chromatographic Analysis of Vitamin E in Microencapsulated Fabric by Foulard

Initial active ingredient amount: The bigger capsule sizes, capsule B and C, have a higher myritol 318 coconut oil and vitamin E amount (recipe 4 and recipe 7) than that of recipe 1 with the smaller capsule size, capsule A. In comparison all above recipes, two parameters;

- Initial active ingredient amount in the capsules by weight percentage and

- The better lost index could be obtained only in recipe 7 in foulard applications.

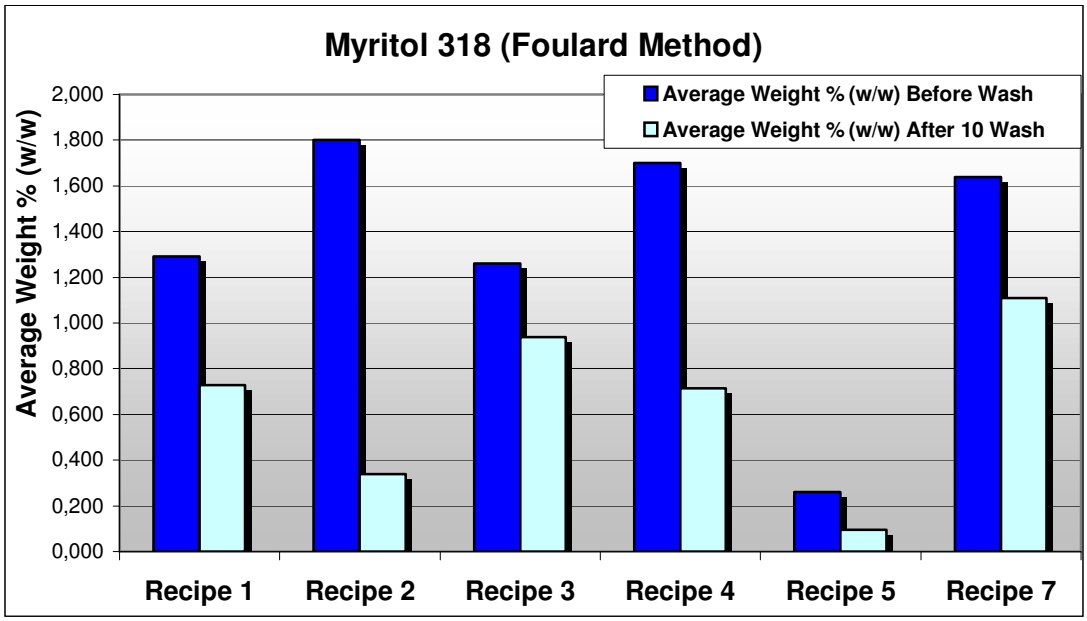


Fig. 4.9: Gas-chromatographic Analysis of Myritol 318 Coconut Oil in Microencapsulated Fabric by Foulard

On the other hand the best value for the lost index belongs to recipe 3. However, the initial average amount % by weight is lower in recipe 3 than that of recipe 4 and recipe 7. Since recipe 3 contains the smallest capsule size, capsule A, the initial active ingredient average amount % (w/w) resulted probably much lower.

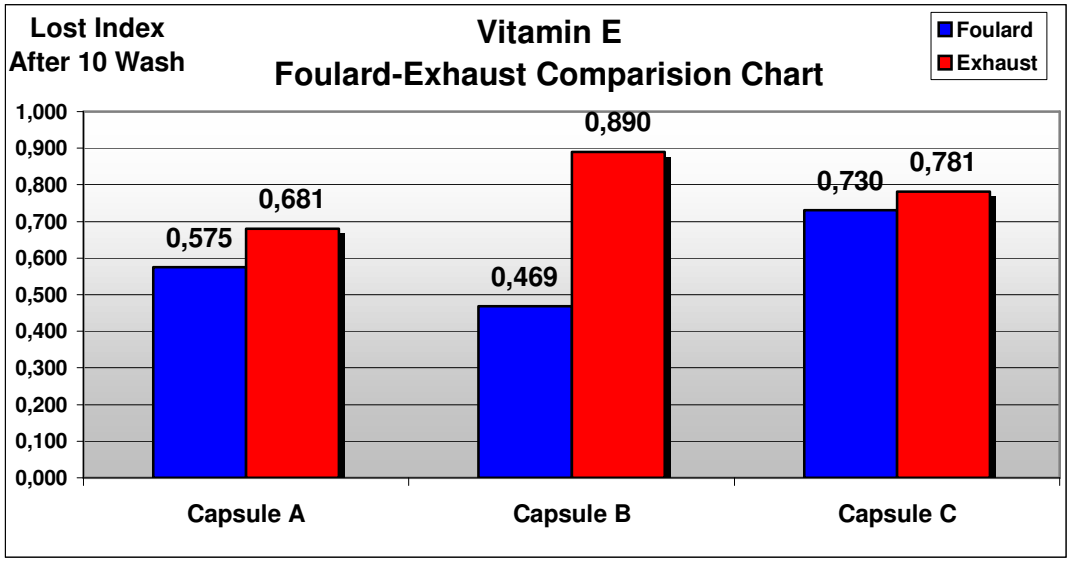


Fig. 4.10: Comparison of Vitamin E Lost Index in Foulard and in Exhaust Method After 10 Wash for 3001A+3002A Binder Combination Used Recipes (Capsule A, B and C)

In Fig 4.10 and Fig. 4.11, it is seen that exhaust method even looked better than foulard method in terms of having a better release rate index. Almost in all capsule sizes, A – B and C, the release rate index values of exhaust method in both vitamin E and myritol 318 coconut oil looks much better than that of foulard one. Beside that, these results were supported with the SEM images in Fig 4.3 – Fig 4.6. Using Nanox 1166 is also played an active role in this result by increasing the initial affinity of the capsules to the fabric. When exhaust SEM images are compared to each other after each washing cycles; before wash, 1 wash, 3 wash, 5 wash, 7 wash, 9 wash and 10 wash; it is also seen that microcapsule durability in exhaust's recipes almost look similar to each others in 4 different recipes regardless of the capsule size.

However, the binder types are limited for exhaust method that can be exhausted easily. Foulard offers a forced application of actives onto the textile, therefore is more controlled method for loading of the textile, while exhaust method is more uncontrolled process. Also, better curing conditions can be obtained in foulard process. Therefore using foulard application for microcapsule treatment is more effective and easily controllable than that of exhaust method. Also, practically, in foulard process, a continue application and conditions can be kept much better to gain consistent quality.

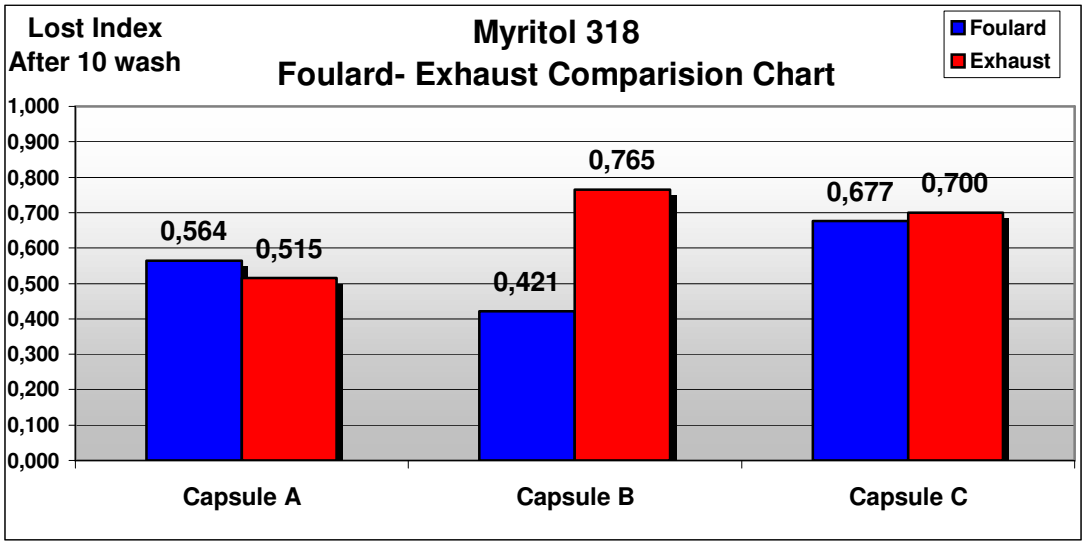
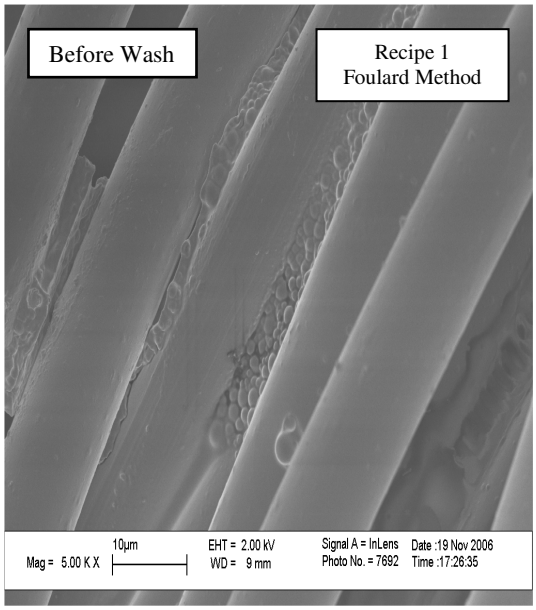
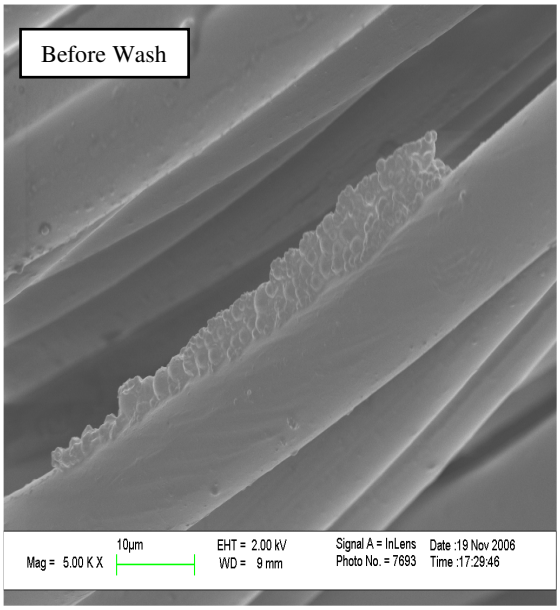
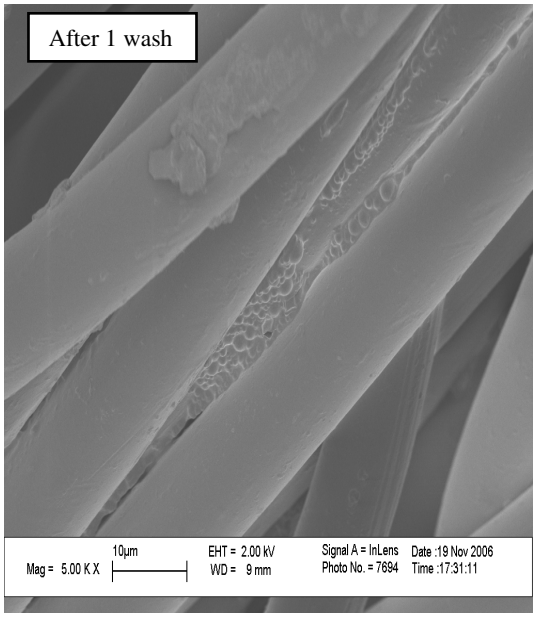


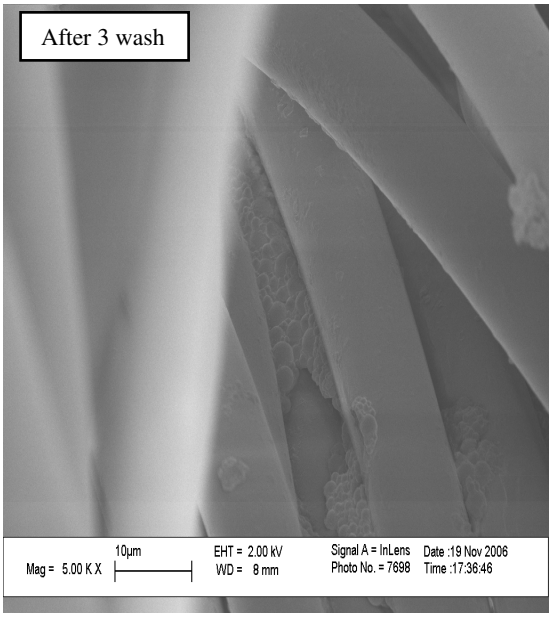
Fig. 4.11: Comparison of Myritol 318 Coconut Oil Lost Index in Foulard and in Exhaust Method After 10 Wash for 3001A+3002A Binder Combination Used Recipes (Capsule A, B and C)

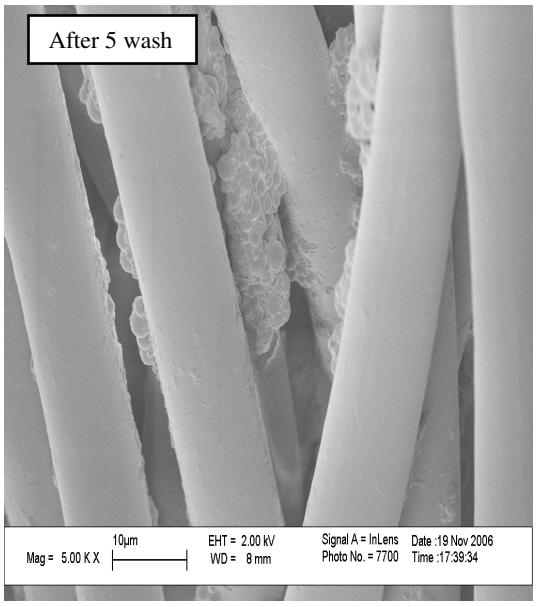
Fig 4.10 and 4.11 shows that capsule size C have high lost indexes for both foulard and exhaust and capsule B has the highest lost index for exhaust method.

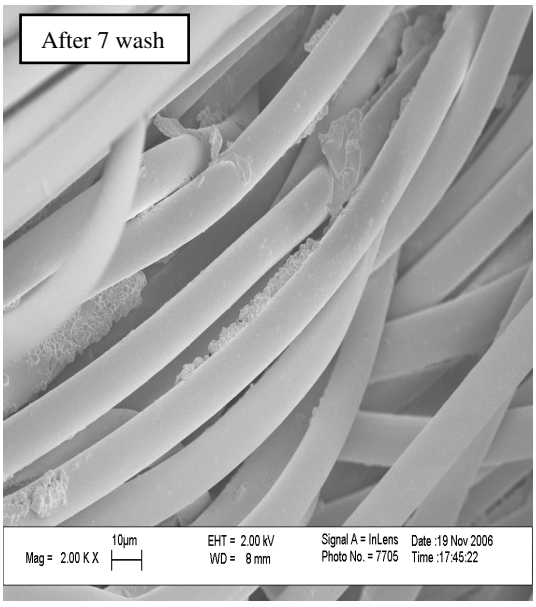

Before Wash
Recipe 1
Foulard Method
10µm
Mag = 5.00 K X
EHT = 2.00 kV
WD = 9 mm
Signal A = InLens
Photo No. = 7692
Date :19 Nov 2006
Time :17:26:35


Before Wash
10µm
Mag = 5.00 K X
EHT = 2.00 kV
WD = 9 mm
Signal A = InLens
Photo No. = 7693
Date :19 Nov 2006
Time :17:29:46


After 1 wash
10µm
Mag = 5.00 K X
EHT = 2.00 kV
WD = 9 mm
Signal A = InLens
Photo No. = 7694
Date :19 Nov 2006
Time :17:31:11


After 3 wash
10µm
Mag = 5.00 K X
EHT = 2.00 kV
WD = 8 mm
Signal A = InLens
Photo No. = 7698
Date :19 Nov 2006
Time :17:36:46


After 5 wash
10µm
Mag = 5.00 K X
EHT = 2.00 kV
WD = 8 mm
Signal A = InLens
Photo No. = 7700
Date :19 Nov 2006
Time :17:39:34


After 7 wash
10µm
Mag = 2.00 K X
EHT = 2.00 kV
WD = 8 mm
Signal A = InLens
Photo No. = 7705
Date :19 Nov 2006
Time :17:45:22

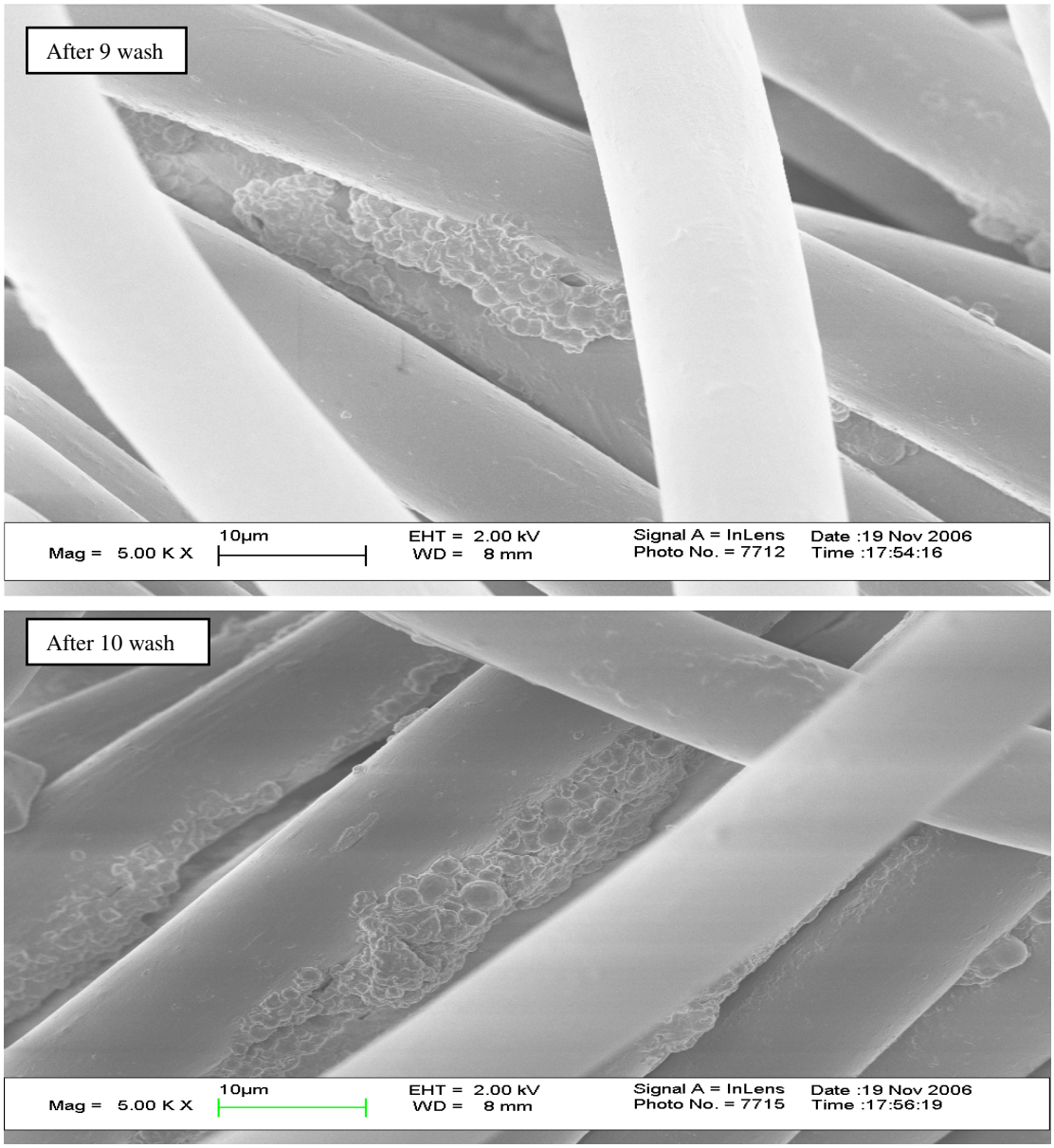
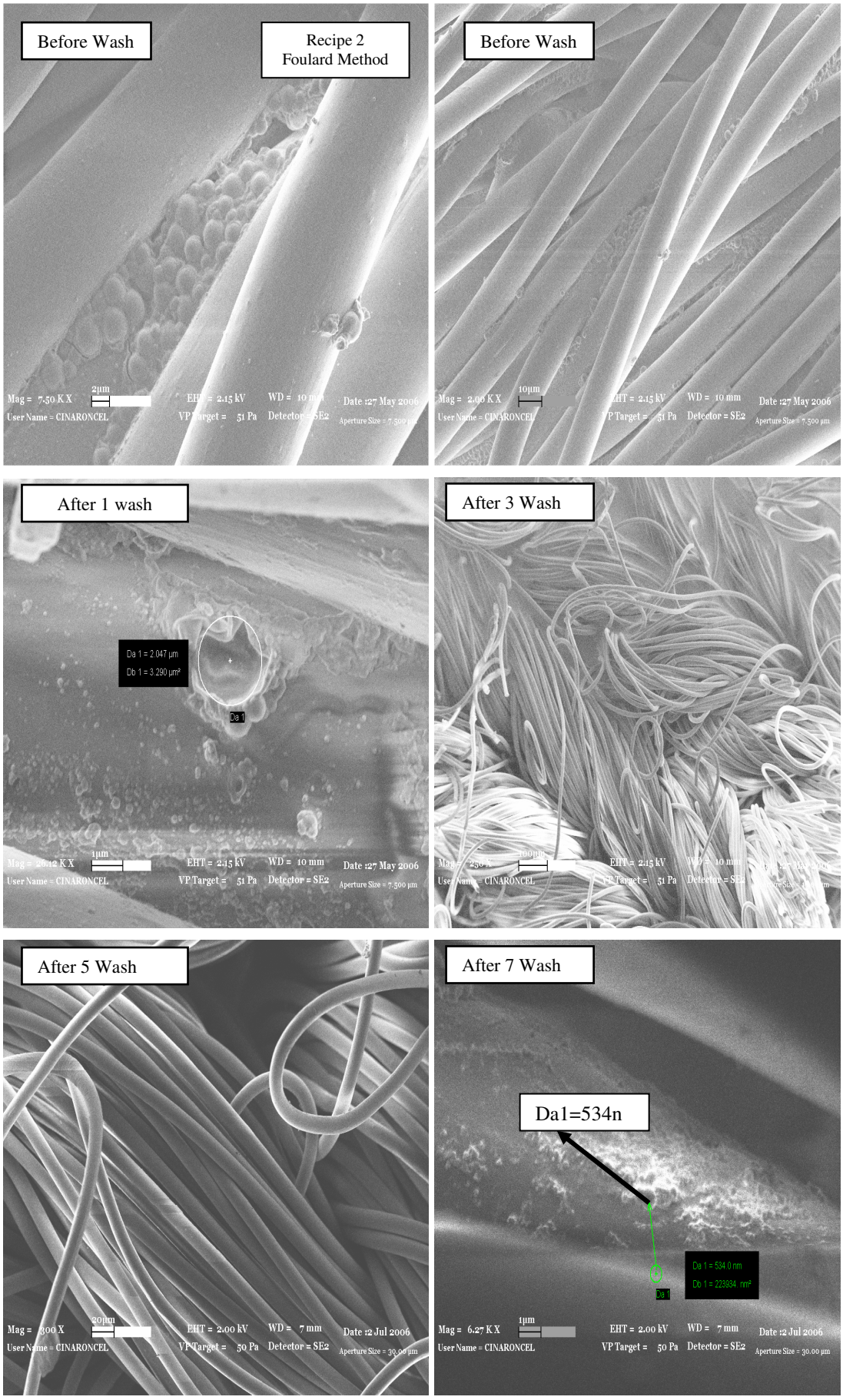


Fig. 4.12: Recipe 1. Foulard Process

Fig 4.12 shows the SEM images of the fabrics processed with Recipe 1 before and after each wash cycle. After each wash cycles, microcapsules are clearly observed in all images in this recipe. They formed groups like a bunch of grapes. The shape of the microcapsules is totally same when compared before and after wash samples with each other.


Before Wash
Recipe 2
Foulard Method
Before Wash
After 1 wash
After 3 Wash
After 5 Wash
After 7 Wash
Da1=534n

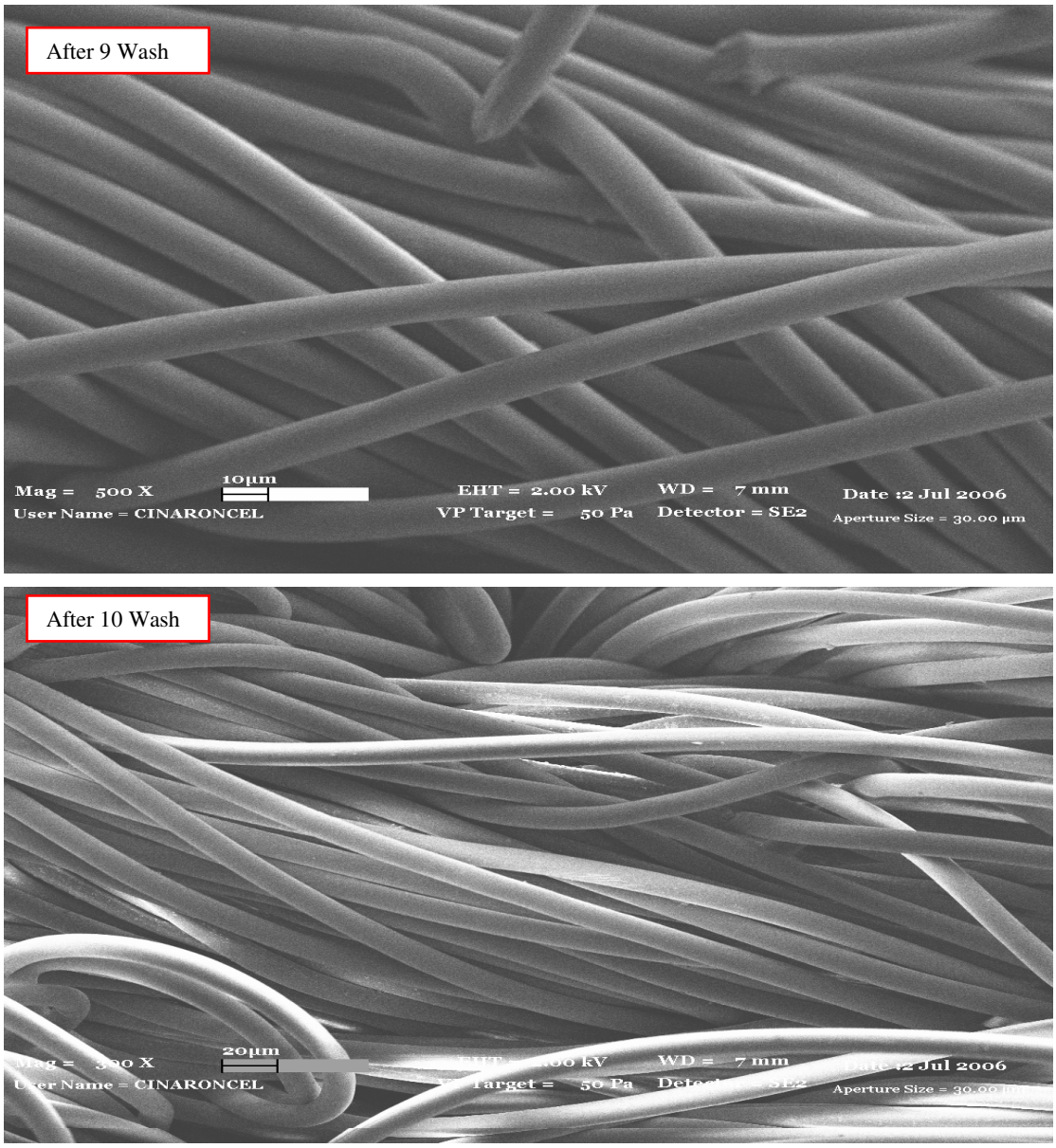
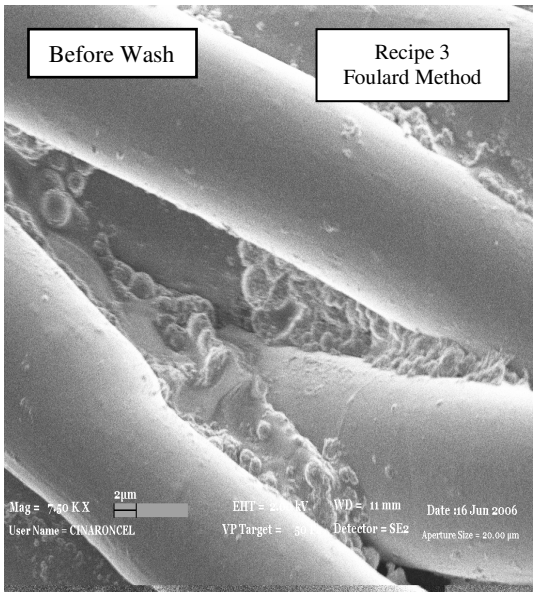
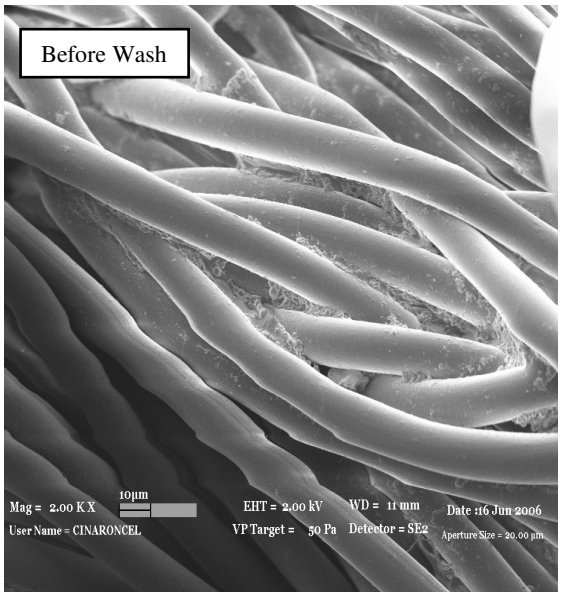
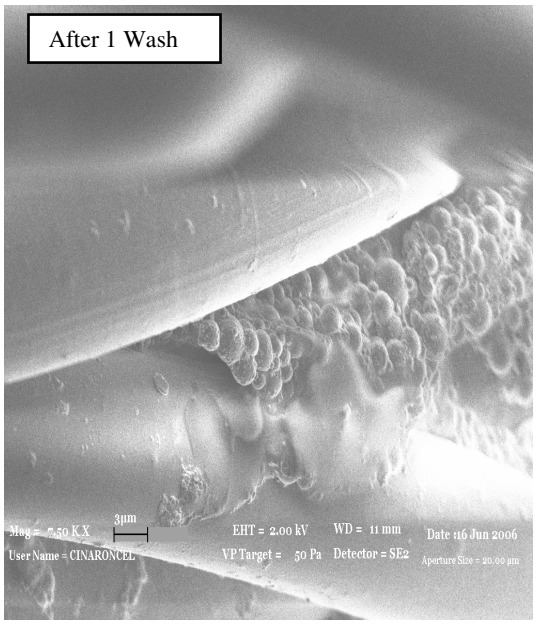


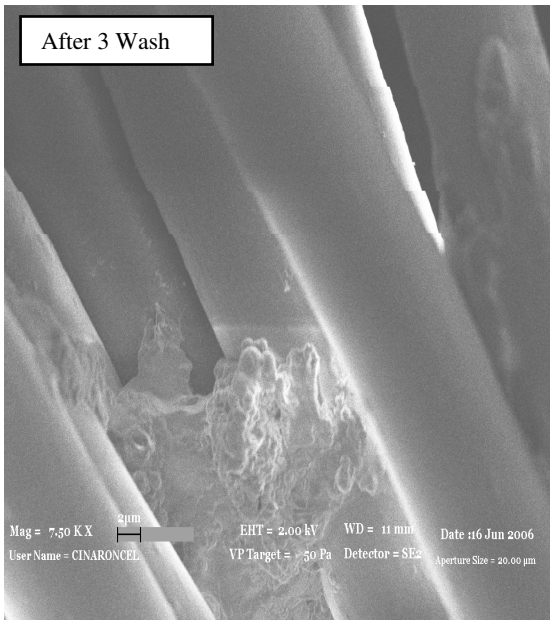
Fig. 4.13: Recipe 2. Foulard Process

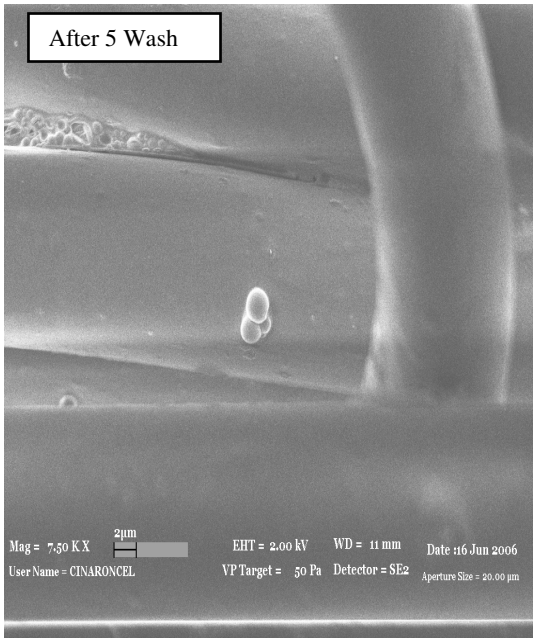
Figure 4.13 shows the SEM images of the samples with Recipe 2. From SEM images, it can be easily seen that the microcapsule amounts are less than Recipe 1 at before and after further washing cycles in Recipe 2. Although there are many capsules before wash; after three washes, most of the capsules are disappeared. The average capsule mean diameter of this recipe was 2-3 µm in capsule A. However, SEM images after 7 wash cycles, the visible microcapsule mean diameter is recorded as 534 nm, which is quite smaller than the average capsule mean diameter. This is also proving us the highest portion of the capsules lost happened after 3rd wash cycles. All these images seen in Fig. 4.13 are also supported by the results of gas chromatogram listed in Table 4.3 and 4.4.

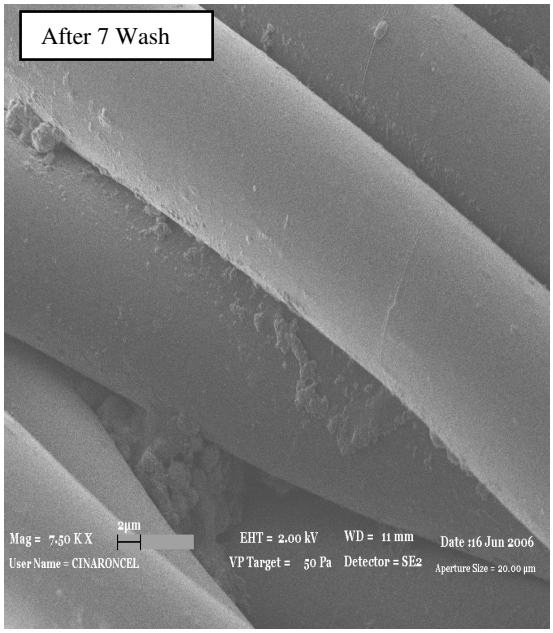

Before Wash
Recipe 3
Foulard Method
2µm
Mag = 7.50 K X
User Name = CINARONCEL
WD = 11 mm
Date :16 Jun 2006
Detector = SE2
Aperture Size = 20.00 µm


Before Wash
10µm
Mag = 2.00 K X
User Name = CINARONCEL
EHT = 2.00 kV
WD = 11 mm
VP Target = 50 Pa
Detector = SE2
Date :16 Jun 2006
Aperture Size = 20.00 µm


After 1 Wash
3µm
Mag = 7.50 K X
User Name = CINARONCEL
EHT = 2.00 kV
WD = 11 mm
VP Target = 50 Pa
Detector = SE2
Date :16 Jun 2006
Aperture Size = 20.00 µm


After 3 Wash
2µm
Mag = 7.50 K X
User Name = CINARONCEL
EHT = 2.00 kV
WD = 11 mm
VP Target = 50 Pa
Detector = SE2
Date :16 Jun 2006
Aperture Size = 20.00 µm


After 5 Wash
2µm
Mag = 7.50 K X
User Name = CINARONCEL
EHT = 2.00 kV
WD = 11 mm
VP Target = 50 Pa
Detector = SE2
Date :16 Jun 2006
Aperture Size = 20.00 µm


After 7 Wash
2µm
Mag = 7.50 K X
User Name = CINARONCEL
EHT = 2.00 kV
WD = 11 mm
VP Target = 50 Pa
Detector = SE2
Date :16 Jun 2006
Aperture Size = 20.00 µm

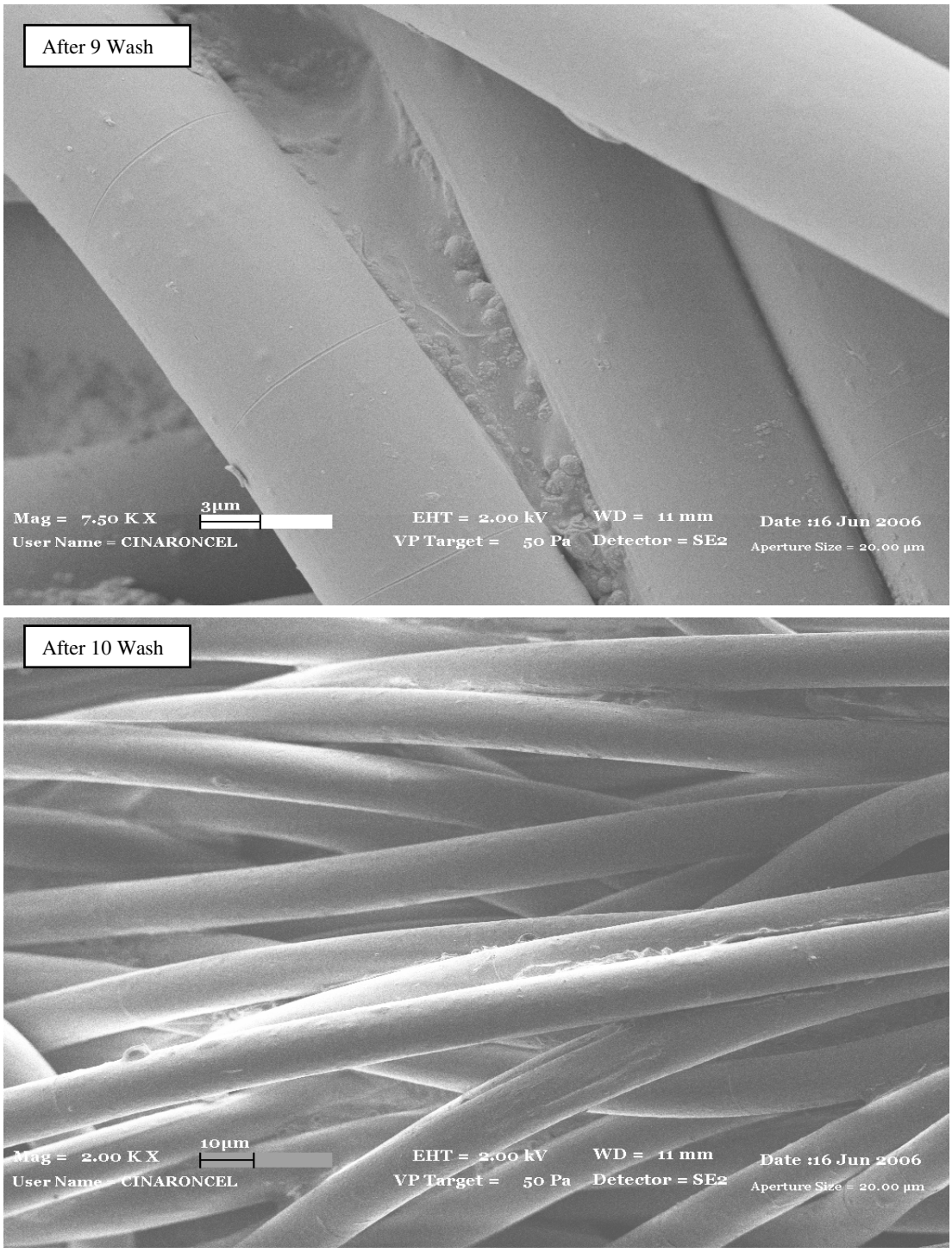
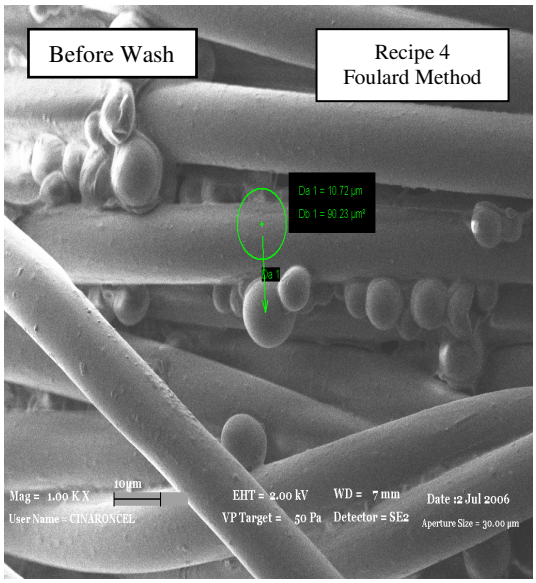
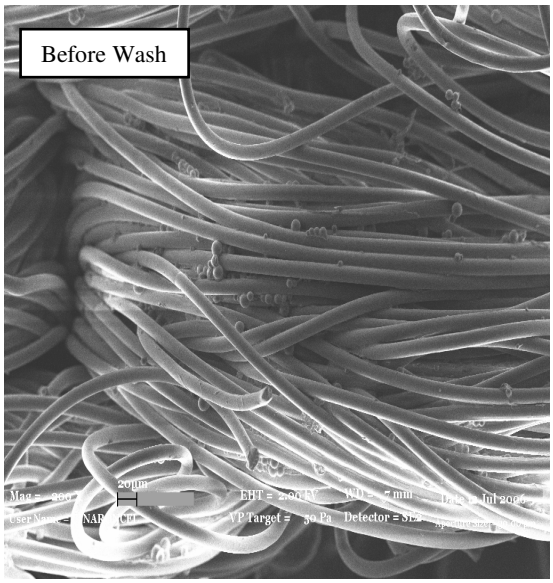
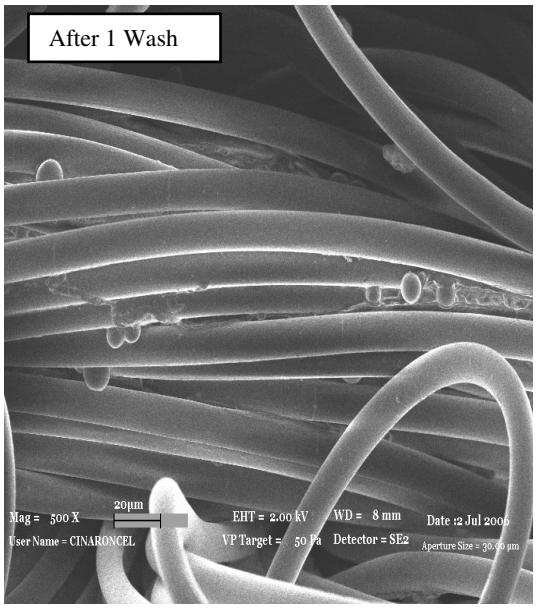


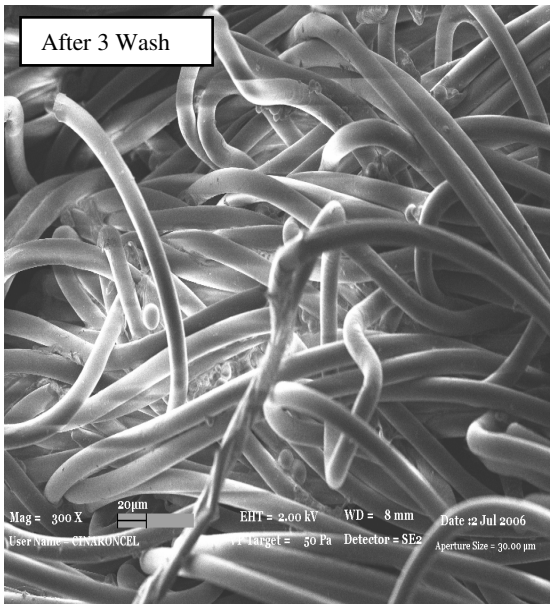
Fig. 4.14: Recipe 3. Foulard Process

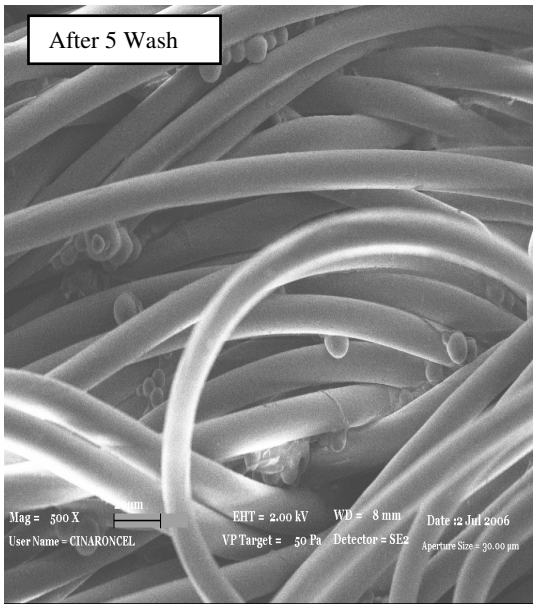
Figure 4.14 shows the SEM images of the samples processed with Recipe 3. It is seen that big amount of capsules are bounded to yarns before wash and after ten wash cycles there are are still microcapsules on the yarn attached by binder 3009A.

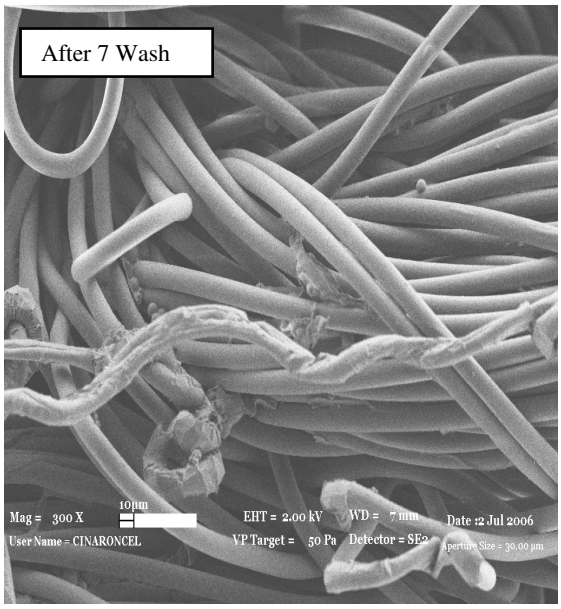

Before Wash
Recipe 4
Foulard Method
Da 1 = 10.72 µm
Db 1 = 90.23 µm²
Mag = 1.00 K X
10µm
EHT = 2.00 kV
WD = 7 mm
Date :2 Jul 2006
User Name = CINARONCEL
VP Target = 50 Pa
Detector = SE2
Aperture Size = 30.00 µm


Before Wash


After 1 Wash
Mag = 500 X
20µm
EHT = 2.00 kV
WD = 8 mm
Date :2 Jul 2006
User Name = CINARONCEL
VP Target = 50 Pa
Detector = SE2
Aperture Size = 30.00 µm


After 3 Wash
Mag = 300 X
20µm
EHT = 2.00 kV
WD = 8 mm
Date :2 Jul 2006
User Name = CINARONCEL
VP Target = 50 Pa
Detector = SE2
Aperture Size = 30.00 µm


After 5 Wash
Mag = 500 X
EHT = 2.00 kV
WD = 8 mm
Date :2 Jul 2006
User Name = CINARONCEL
VP Target = 50 Pa
Detector = SE2
Aperture Size = 30.00 µm


After 7 Wash
Mag = 300 X
10µm
EHT = 2.00 kV
WD = 7 mm
Date :2 Jul 2006
User Name = CINARONCEL
VP Target = 50 Pa
Detector = SE2
Aperture Size = 30.00 µm

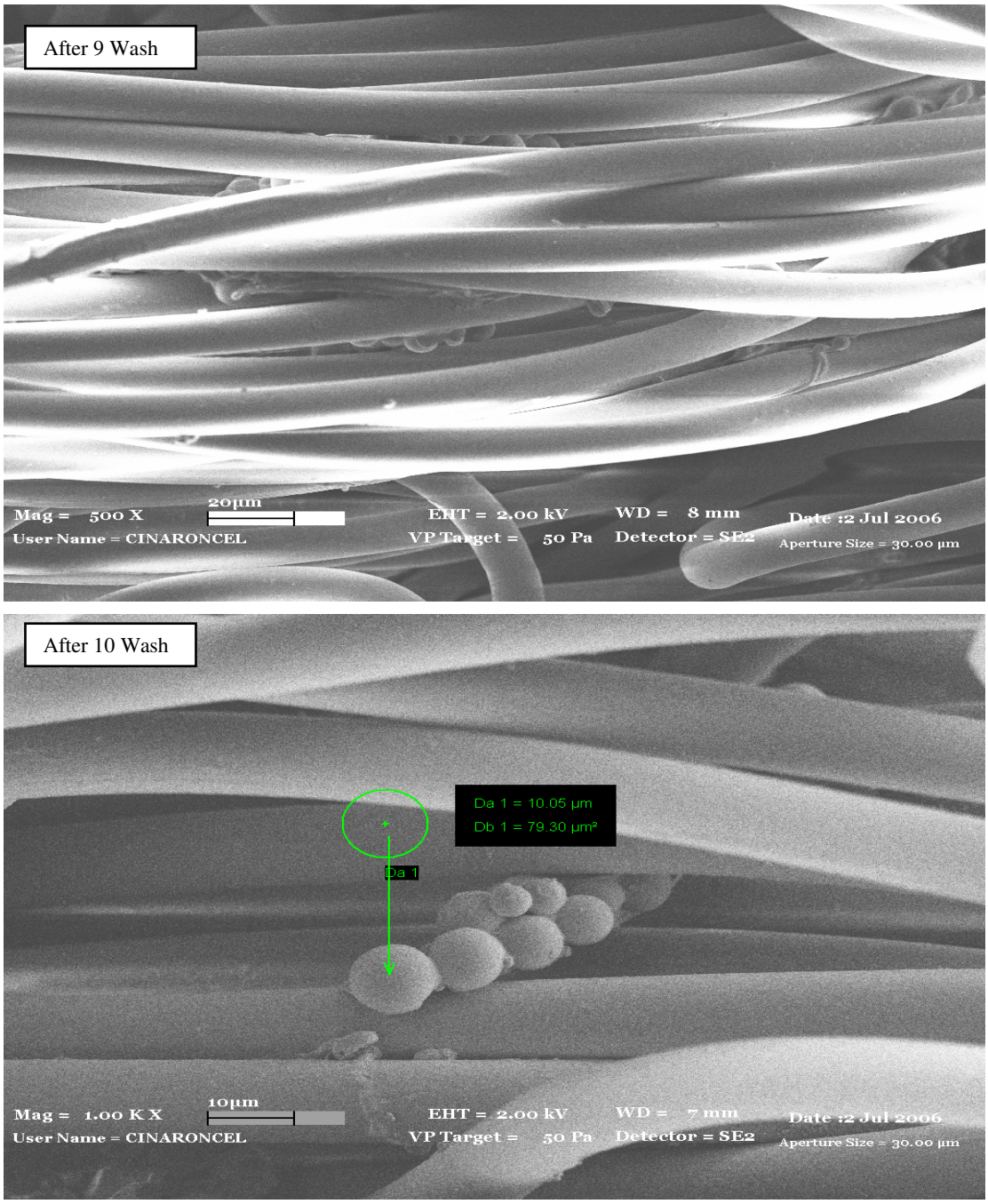
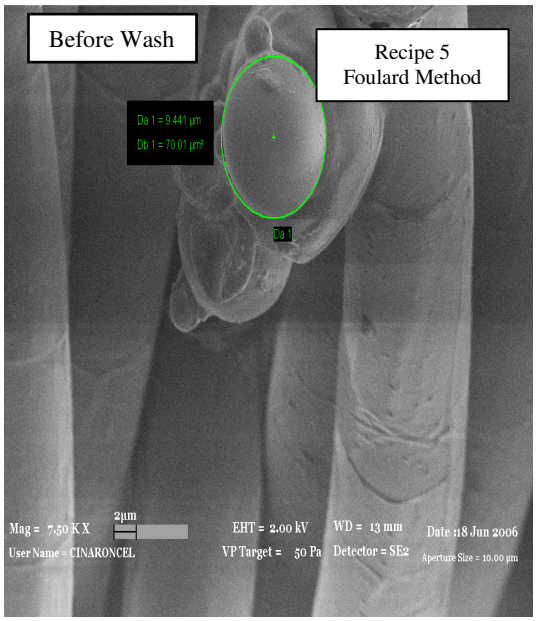
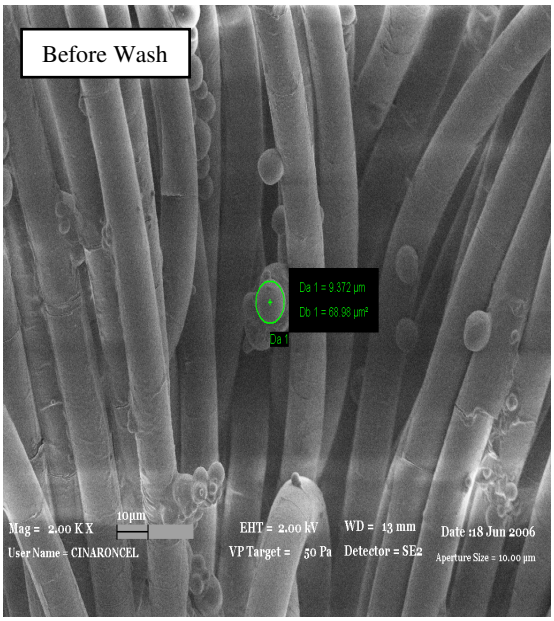
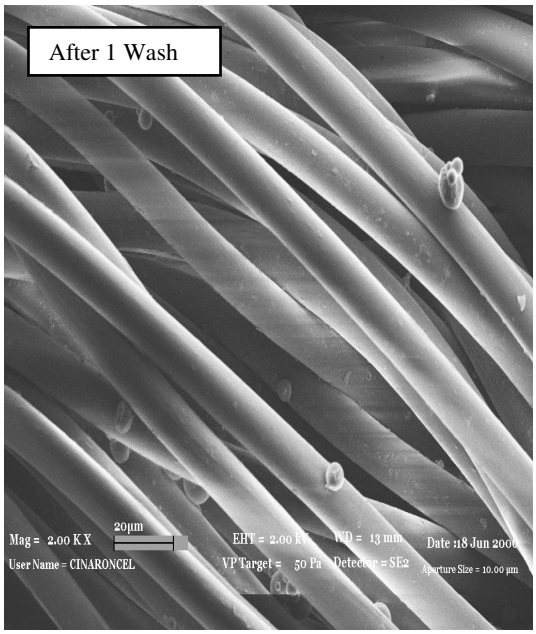


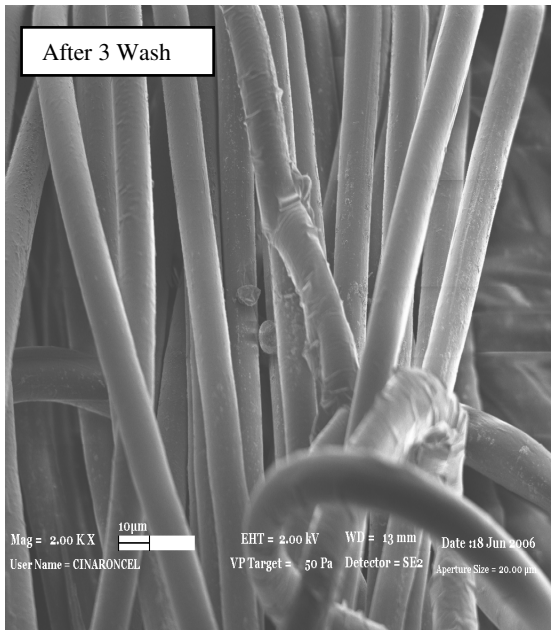
Fig. 4.15: Recipe 4. Foulard Process

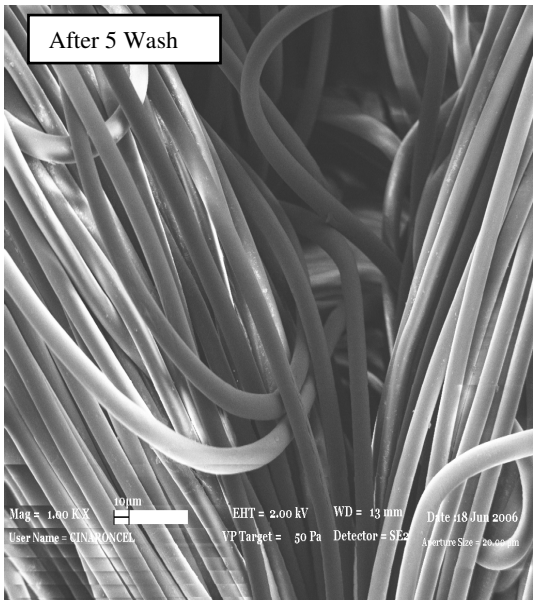
Fig 4.15 shows the SEM images of the samples processed with Recipe 4. This is the biggest capsule size used in this study. The capsules are much evenly distributed than the other recipes. It is seen that after ten washes the microcapsules are not totally destroyed and still the initial size and shape of the capsules could be kept as spherical and as 8-10 µm.

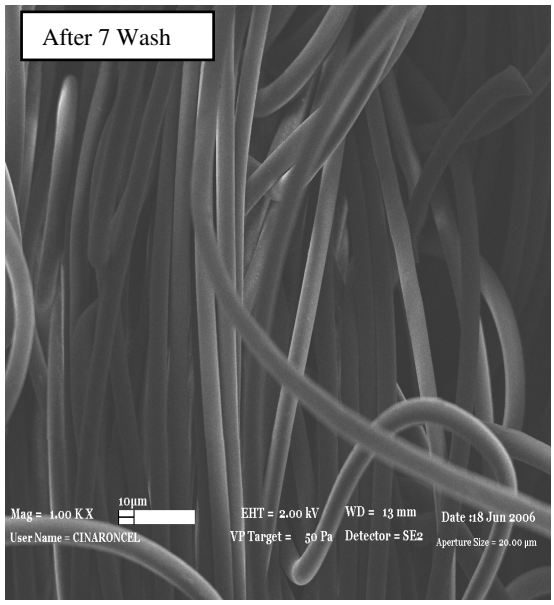

Before Wash
Recipe 5
Foulard Method
Da 1 = 9.441 µm
Db 1 = 70.01 µm²
Da 1
Mag = 7.50 K X
2µm
EHT = 2.00 kV
WD = 13 mm
Date :18 Jun 2006
User Name = CINARONCEL
VP Target = 50 Pa
Detector = SE2
Aperture Size = 10.00 µm


Before Wash
Da 1 = 9.372 µm
Db 1 = 68.98 µm²
Da 1
Mag = 2.00 K X
10µm
EHT = 2.00 kV
WD = 13 mm
Date :18 Jun 2006
User Name = CINARONCEL
VP Target = 50 Pa
Detector = SE2
Aperture Size = 10.00 µm


After 1 Wash
Mag = 2.00 K X
20µm
EHT = 2.00 kV
WD = 13 mm
Date :18 Jun 2006
User Name = CINARONCEL
VP Target = 50 Pa
Detector = SE2
Aperture Size = 10.00 µm


After 3 Wash
Mag = 2.00 K X
10µm
EHT = 2.00 kV
WD = 13 mm
Date :18 Jun 2006
User Name = CINARONCEL
VP Target = 50 Pa
Detector = SE2
Aperture Size = 20.00 µm


After 5 Wash
Mag = 1.00 K X
10µm
EHT = 2.00 kV
WD = 13 mm
Date :18 Jun 2006
User Name = CINARONCEL
VP Target = 50 Pa
Detector = SE2
Aperture Size = 20.00 µm


After 7 Wash
Mag = 1.00 K X
10µm
EHT = 2.00 kV
WD = 13 mm
Date :18 Jun 2006
User Name = CINARONCEL
VP Target = 50 Pa
Detector = SE2
Aperture Size = 20.00 µm

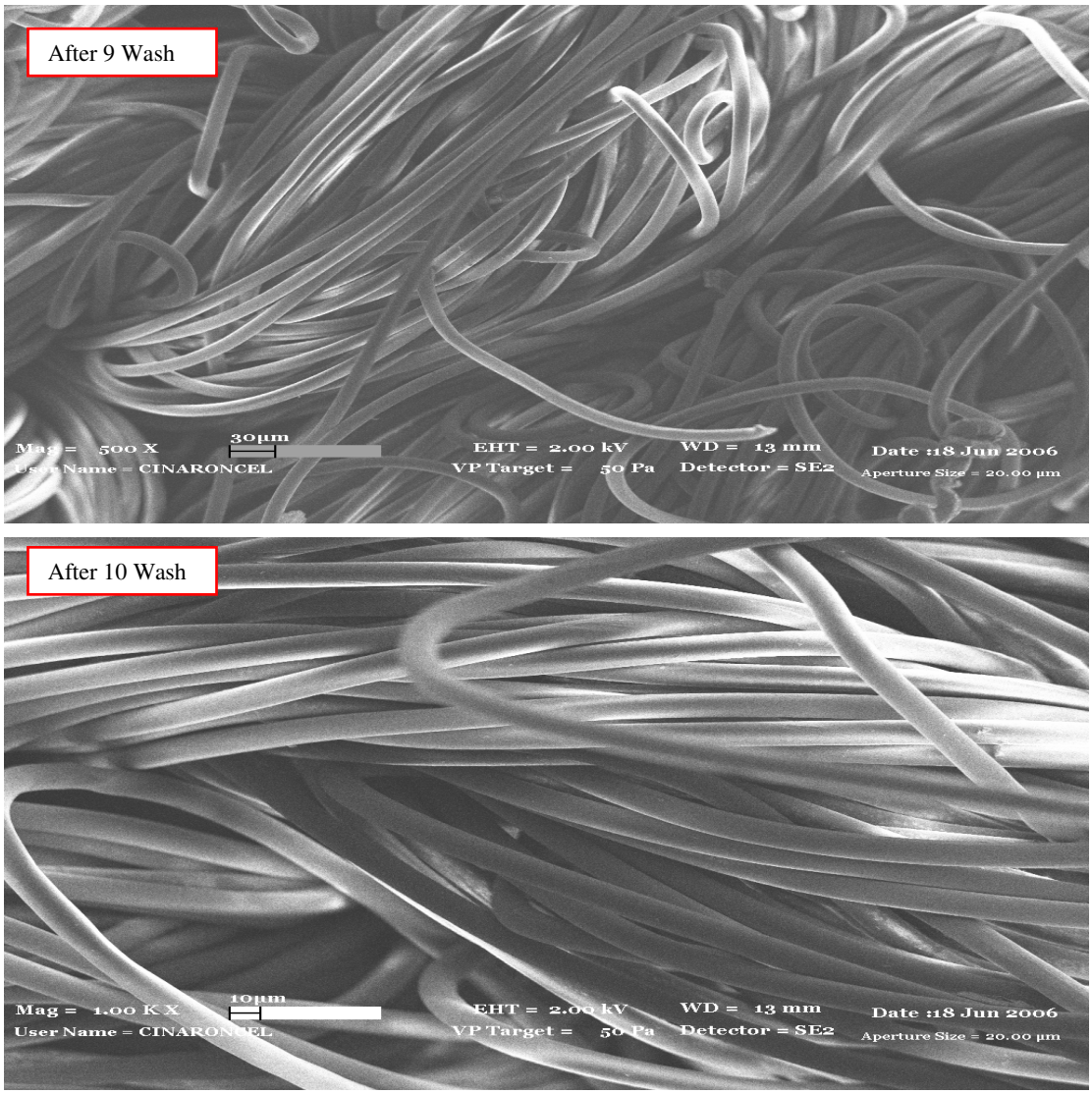
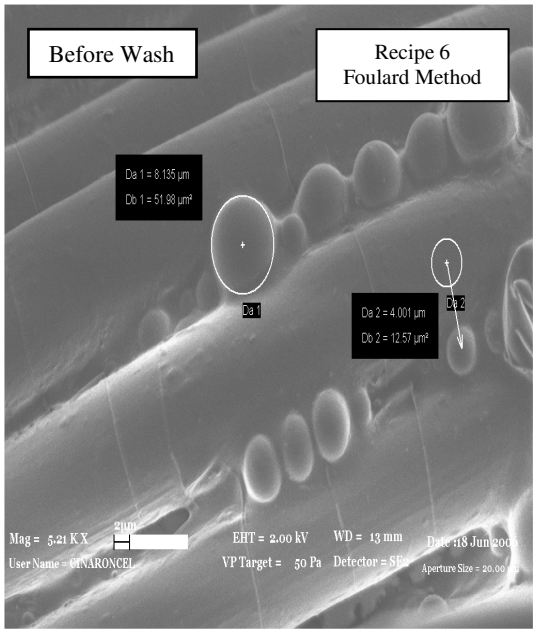
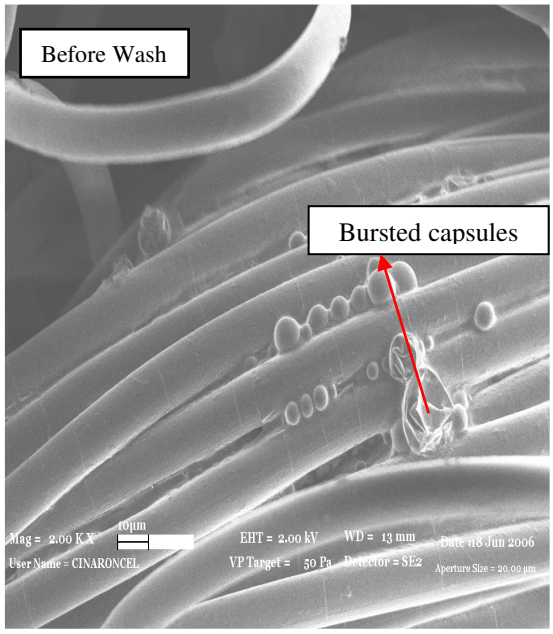
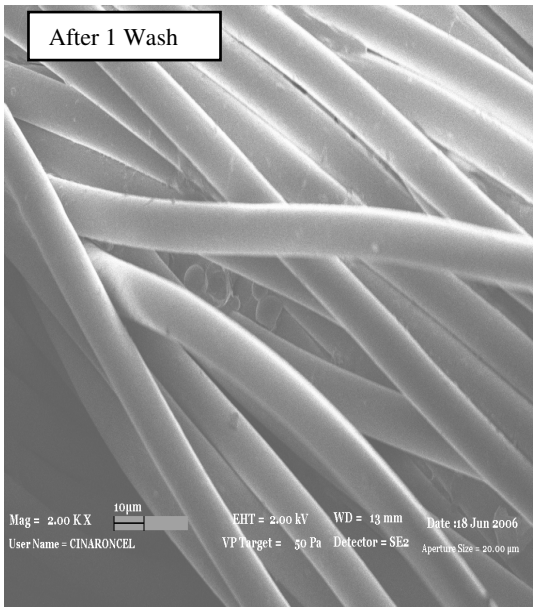


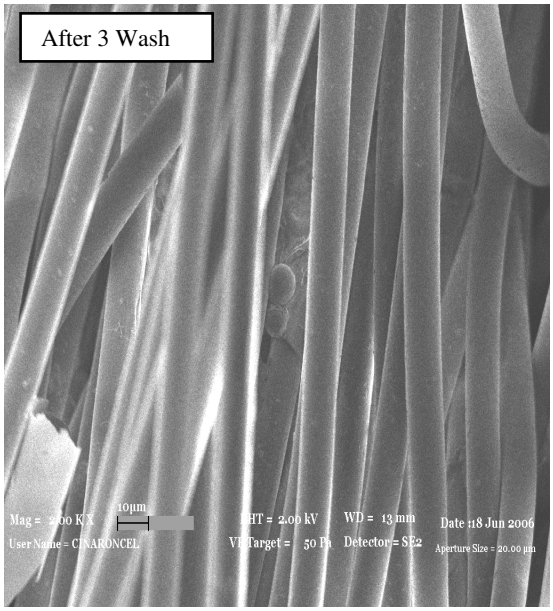
Fig. 4.16: Recipe 5. Foulard Process

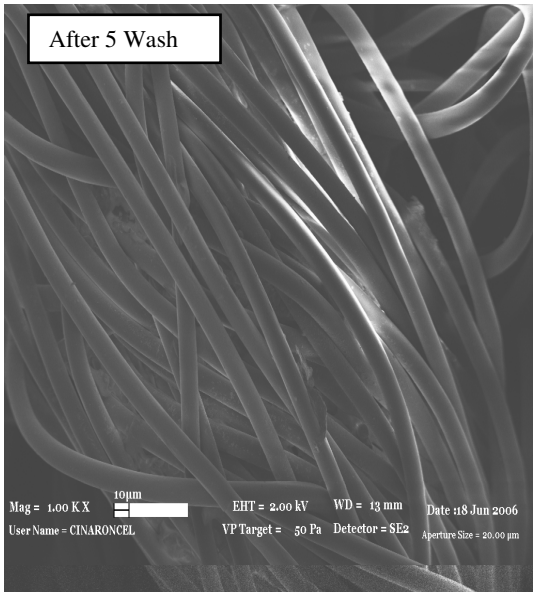
Fig 4.16 shows the SEM images of Recipe 5 taken before wash and after each wash cycles. The gas chromatographic results are confirmed by the SEM images in Fig 4.16. Before wash, we can see the microcapsules bounded the yarns but after 1 wash and onwards the microcapsules are mostly disappeared. After 5 washes there isn't any microcapsule on the fabrics, maybe some very small sized amounts kept between the yarns but cannot be seen under SEM. If we make comparison between Fig 4.13 with Fig 4.16 in Table 4.3 and 4.4, it is seen that more capsules are bounded on fibers with Recipe 2 than Recipe 5.

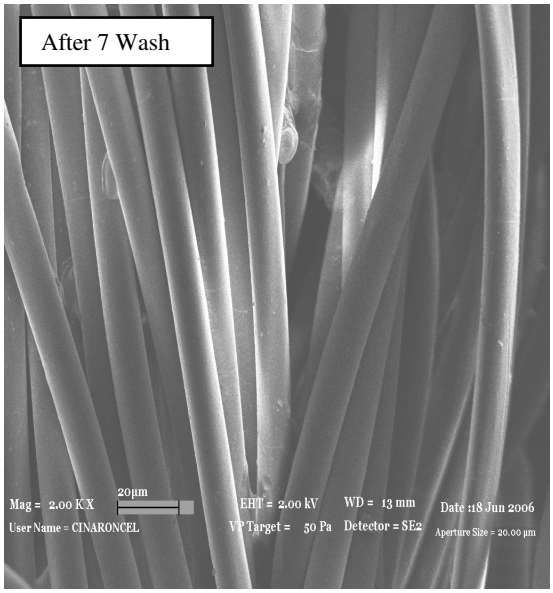

Before Wash
Recipe 6
Foulard Method
Da 1 = 8.135 µm
Db 1 = 51.98 µm²
Da 1
Da 2 = 4.001 µm
Db 2 = 12.57 µm²
Da 2
Mag = 5.21 K X
2µm
EHT = 2.00 kV
WD = 13 mm
VP Target = 50 Pa
Detector = SE2
Date :18 Jun 2006
User Name = CINARONCEL
Aperture Size = 20.00 µm


Before Wash
Bursted capsules
Mag = 2.00 K X
10µm
EHT = 2.00 kV
WD = 13 mm
VP Target = 50 Pa
Detector = SE2
Date :18 Jun 2006
User Name = CINARONCEL
Aperture Size = 20.00 µm


After 1 Wash
Mag = 2.00 K X
10µm
EHT = 2.00 kV
WD = 13 mm
VP Target = 50 Pa
Detector = SE2
Date :18 Jun 2006
User Name = CINARONCEL
Aperture Size = 20.00 µm


After 3 Wash
10µm
EHT = 2.00 kV
WD = 13 mm
VP Target = 50 Pa
Detector = SE2
Date :18 Jun 2006
User Name = CINARONCEL
Aperture Size = 20.00 µm


After 5 Wash
Mag = 1.00 K X
10µm
EHT = 2.00 kV
WD = 13 mm
VP Target = 50 Pa
Detector = SE2
Date :18 Jun 2006
User Name = CINARONCEL
Aperture Size = 20.00 µm


After 7 Wash
Mag = 2.00 K X
20µm
EHT = 2.00 kV
WD = 13 mm
VP Target = 50 Pa
Detector = SE2
Date :18 Jun 2006
User Name = CINARONCEL
Aperture Size = 20.00 µm

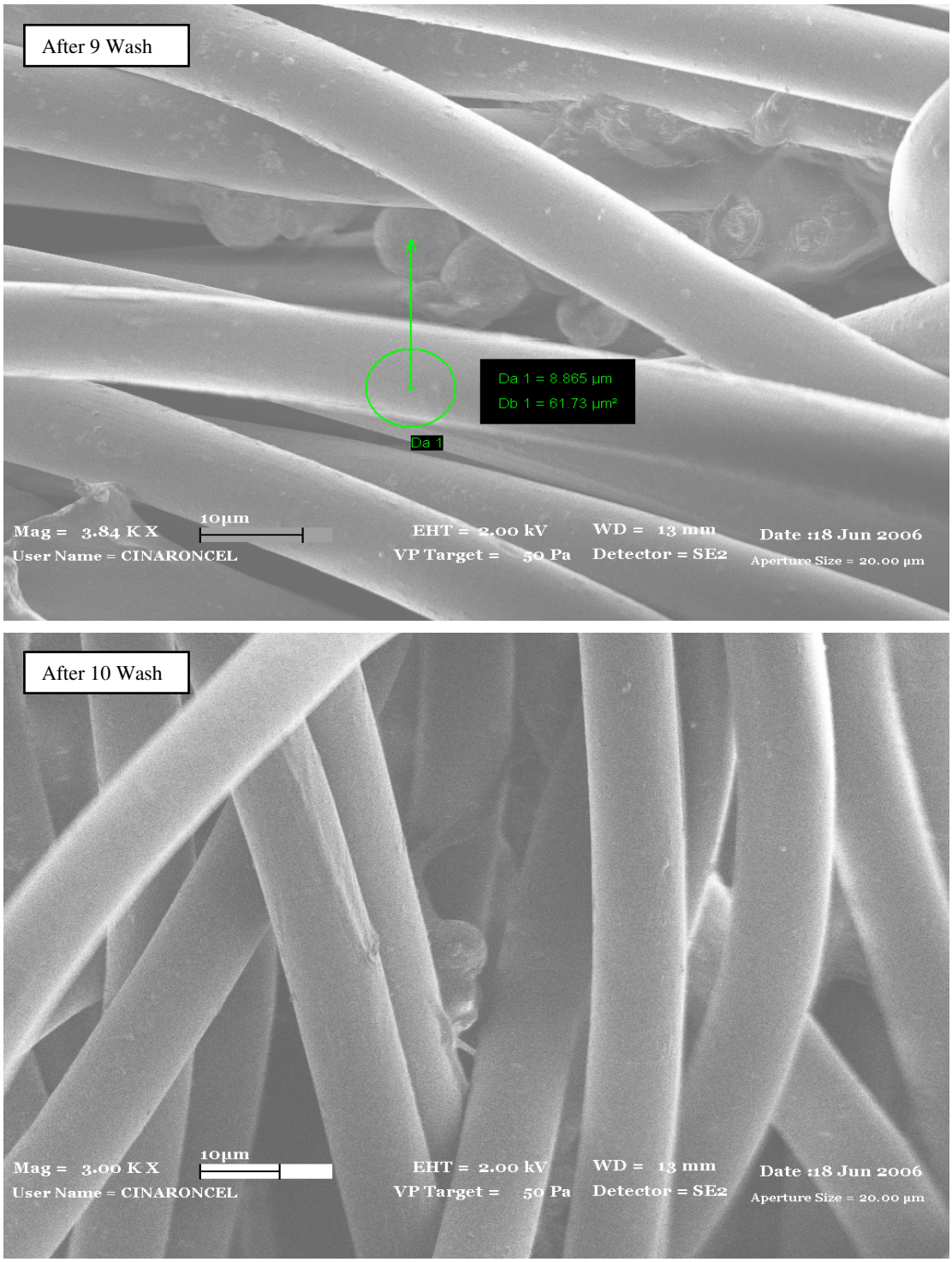
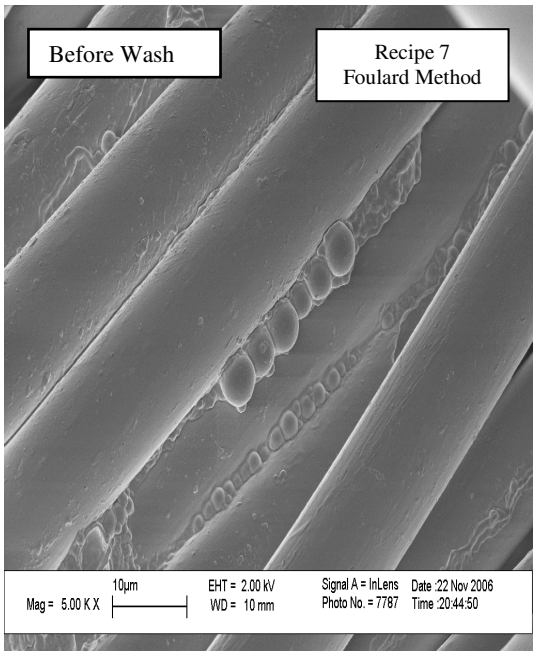
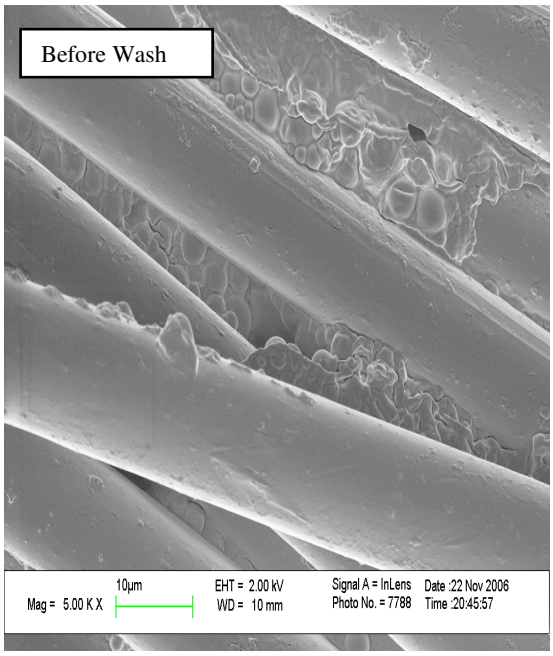
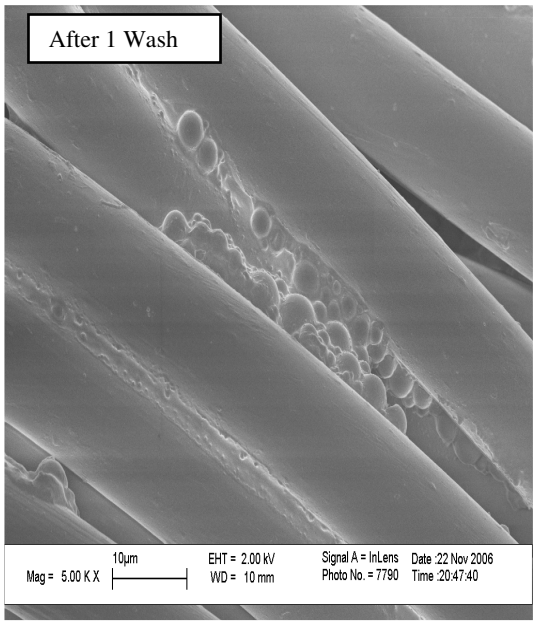


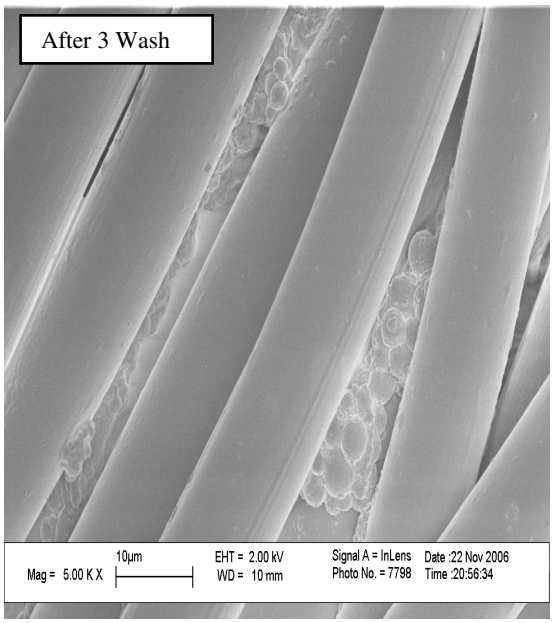
Fig. 4.17: Recipe 6. Foulard Process

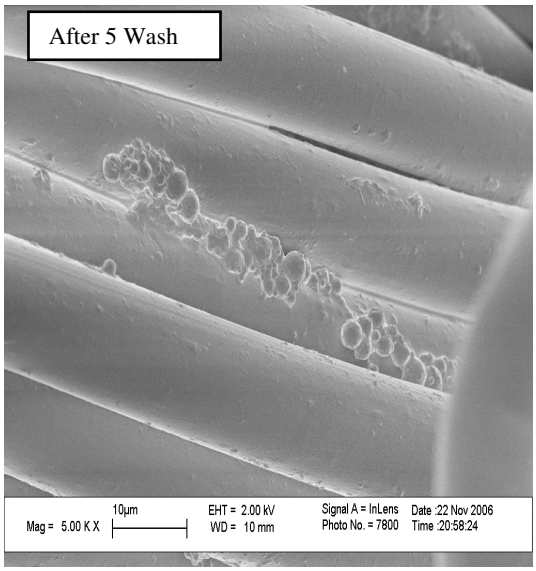
Fig. 4.17 shows the SEM images of samples processed with Recipe 6. We can see the spherical shaped microcapsules on the yarns before wash. After 9 washing cycle, it is seen that there are still microcapsules bounded on yarns, but it is also seen that some of microcapsules destroyed. Similar to Recipe 4, the microcapsules are distributed evenly on to the yarn surface of the fabric in Recipe 6.

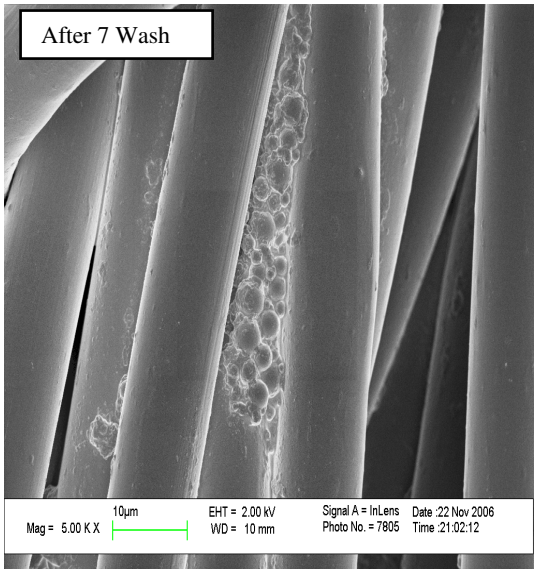

Before Wash
Recipe 7
Foulard Method
10µm
Mag = 5.00 K X
EHT = 2.00 kV
WD = 10 mm
Signal A = InLens
Photo No. = 7787
Date :22 Nov 2006
Time :20:44:50


Before Wash
10µm
Mag = 5.00 K X
EHT = 2.00 kV
WD = 10 mm
Signal A = InLens
Photo No. = 7788
Date :22 Nov 2006
Time :20:45:57


After 1 Wash
10µm
Mag = 5.00 K X
EHT = 2.00 kV
WD = 10 mm
Signal A = InLens
Photo No. = 7790
Date :22 Nov 2006
Time :20:47:40


After 3 Wash
10µm
Mag = 5.00 K X
EHT = 2.00 kV
WD = 10 mm
Signal A = InLens
Photo No. = 7798
Date :22 Nov 2006
Time :20:56:34


After 5 Wash
10µm
Mag = 5.00 K X
EHT = 2.00 kV
WD = 10 mm
Signal A = InLens
Photo No. = 7800
Date :22 Nov 2006
Time :20:58:24


After 7 Wash
10µm
Mag = 5.00 K X
EHT = 2.00 kV
WD = 10 mm
Signal A = InLens
Photo No. = 7805
Date :22 Nov 2006
Time :21:02:12

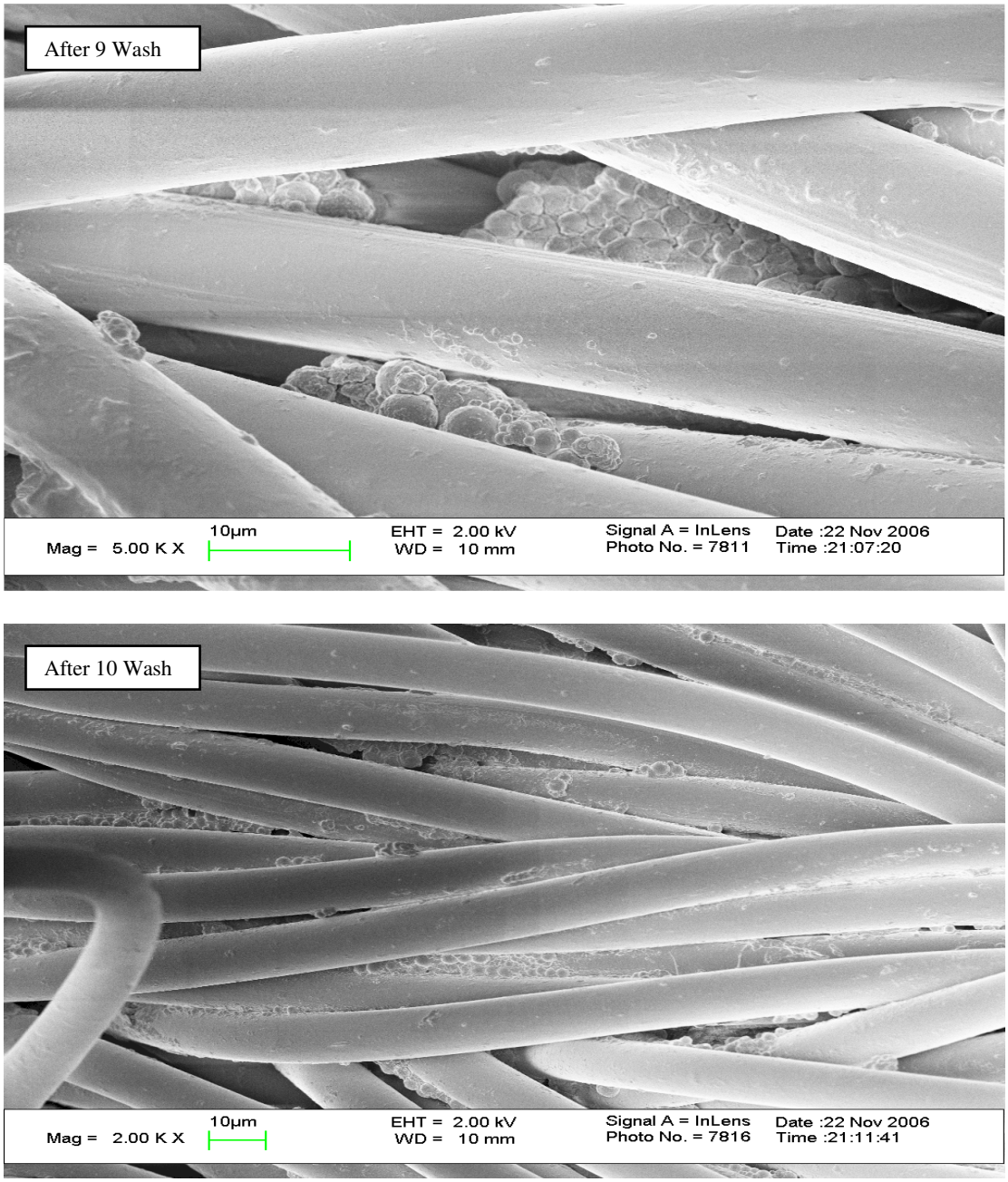
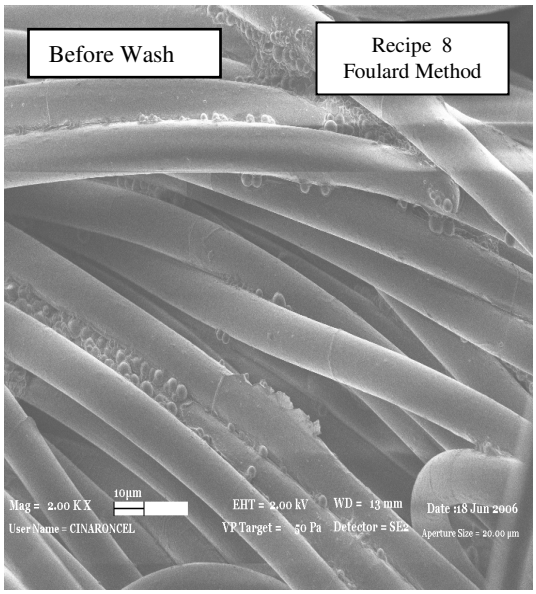
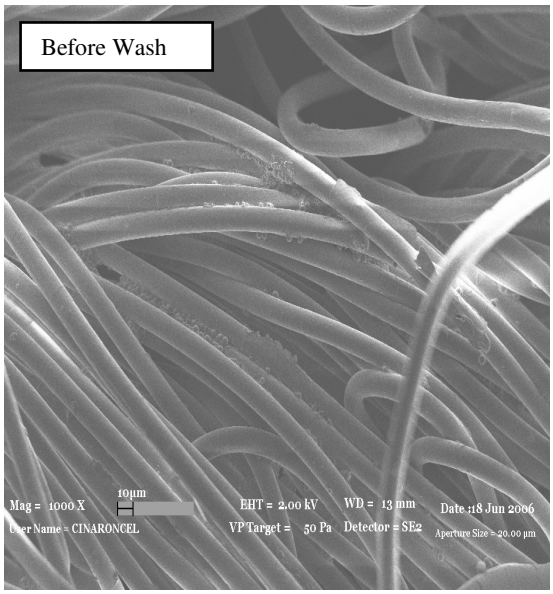
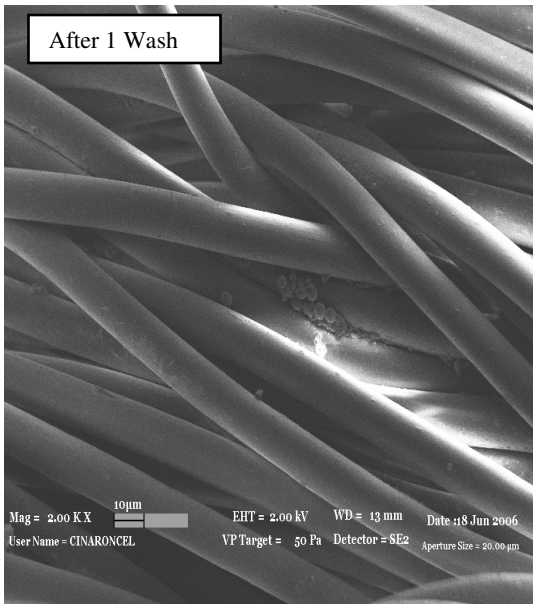


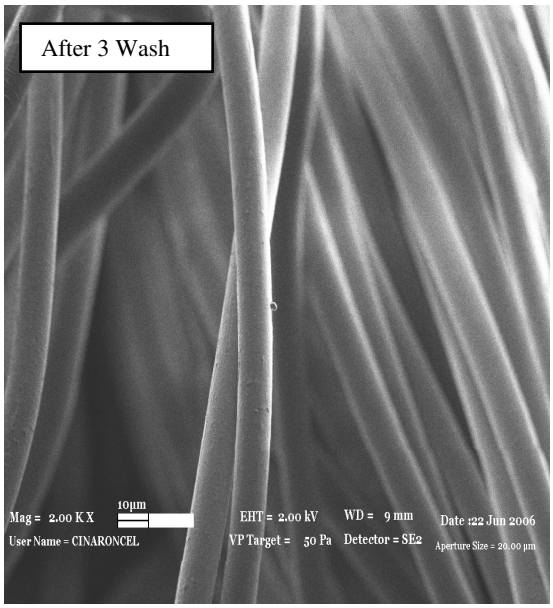
Fig. 4.18: Recipe 7. Foulard Process

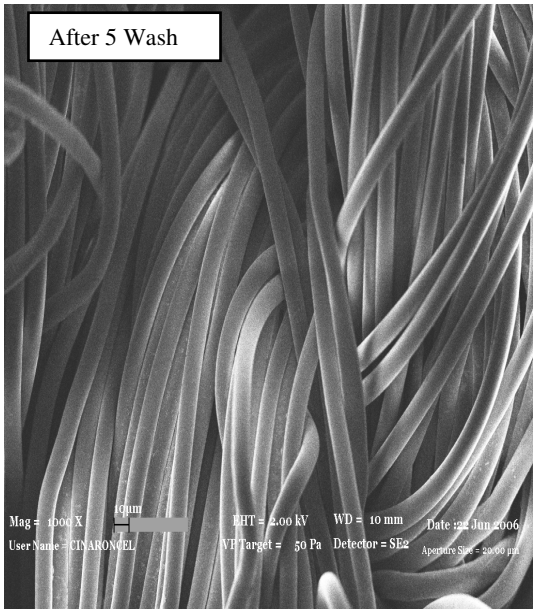
Fig 4.18 shows the SEM images of microcapsules applied on fabric by Recipe 7. The microcapsules are easily seen that are strongly bounded on the yarn before wash and after each wash cycles. Even after 10 wash cycles it is seen that high amount of microcapsules are still bounded on the yarn surface and microcapsules shapes are not damaged and are still in spherical form. This figure confirms the high quality of binder type 3001A+3002A when compared with 3003A.

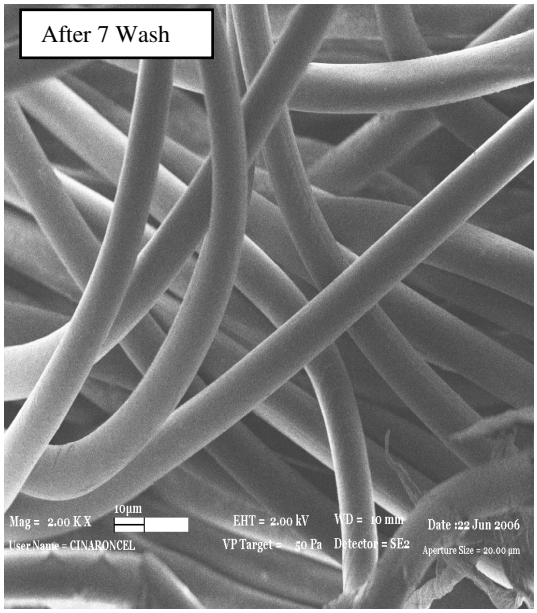

Before Wash
Recipe 8
Foulard Method
Mag = 2.00 K X
10µm
EHT = 2.00 kV
WD = 13 mm
Date :18 Jun 2006
User Name = CINARONCEL
VP Target = 50 Pa
Detector = SE2
Aperture Size = 20.00 µm


Before Wash
Mag = 1000 X
10µm
EHT = 2.00 kV
WD = 13 mm
Date :18 Jun 2006
User Name = CINARONCEL
VP Target = 50 Pa
Detector = SE2
Aperture Size = 20.00 µm


After 1 Wash
Mag = 2.00 K X
10µm
EHT = 2.00 kV
WD = 13 mm
Date :18 Jun 2006
User Name = CINARONCEL
VP Target = 50 Pa
Detector = SE2
Aperture Size = 20.00 µm


After 3 Wash
Mag = 2.00 K X
10µm
EHT = 2.00 kV
WD = 9 mm
Date :22 Jun 2006
User Name = CINARONCEL
VP Target = 50 Pa
Detector = SE2
Aperture Size = 20.00 µm


After 5 Wash
Mag = 1000 X
10µm
EHT = 2.00 kV
WD = 10 mm
Date :22 Jun 2006
User Name = CINARONCEL
VP Target = 50 Pa
Detector = SE2
Aperture Size = 20.00 µm


After 7 Wash
Mag = 2.00 K X
10µm
EHT = 2.00 kV
WD = 10 mm
Date :22 Jun 2006
User Name = CINARONCEL
VP Target = 50 Pa
Detector = SE2
Aperture Size = 20.00 µm

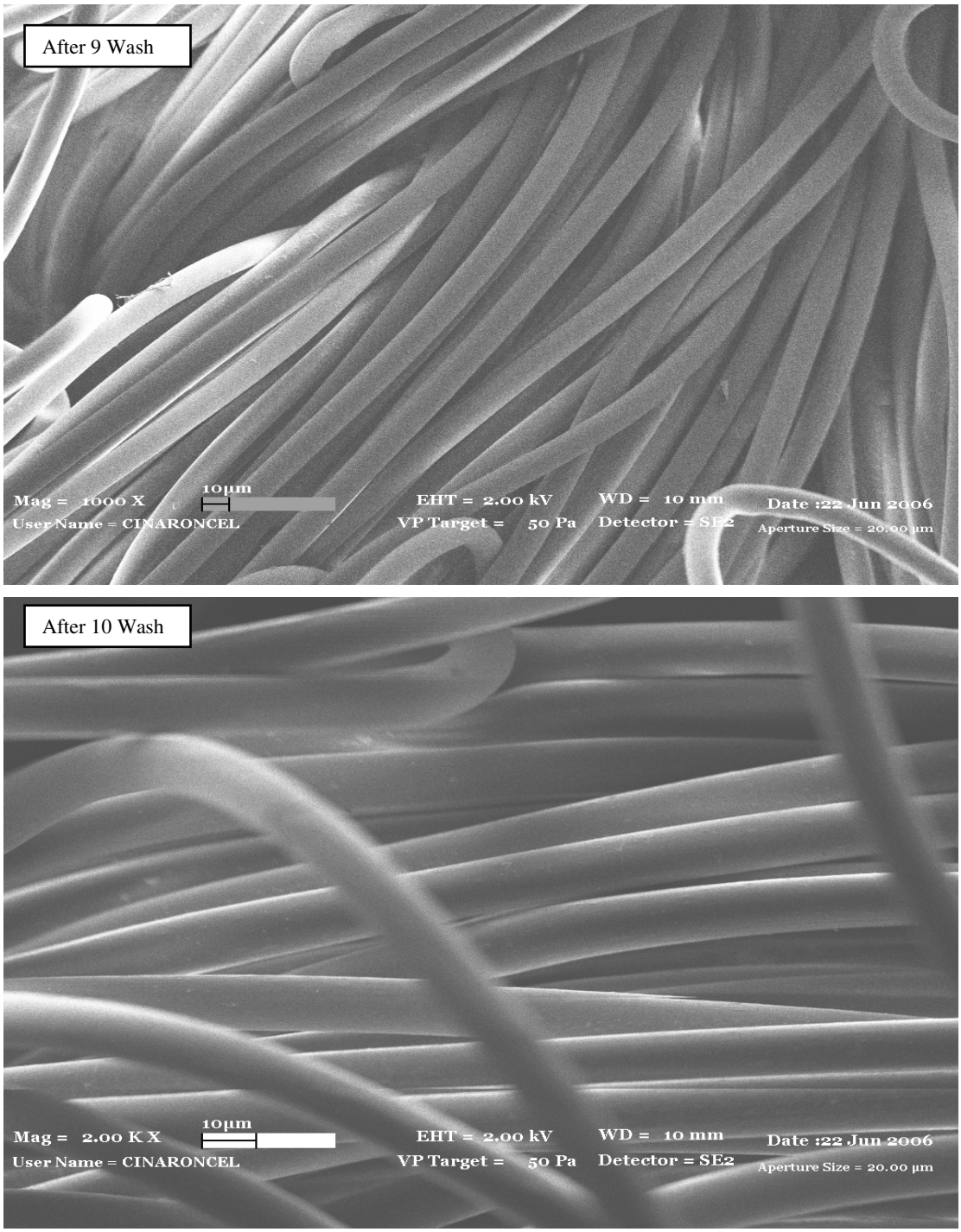
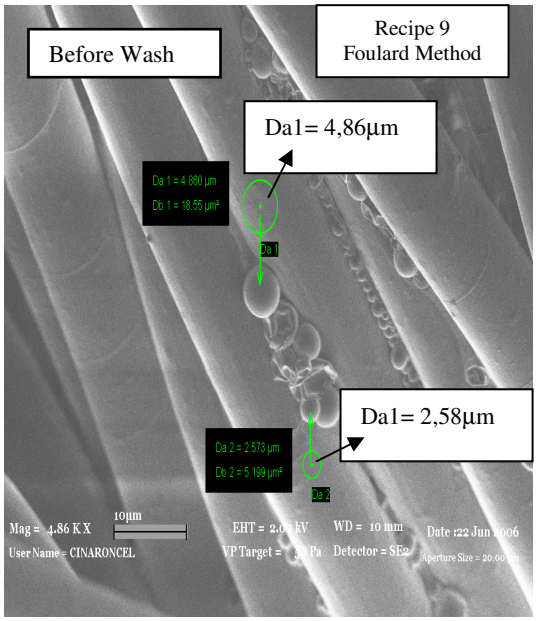
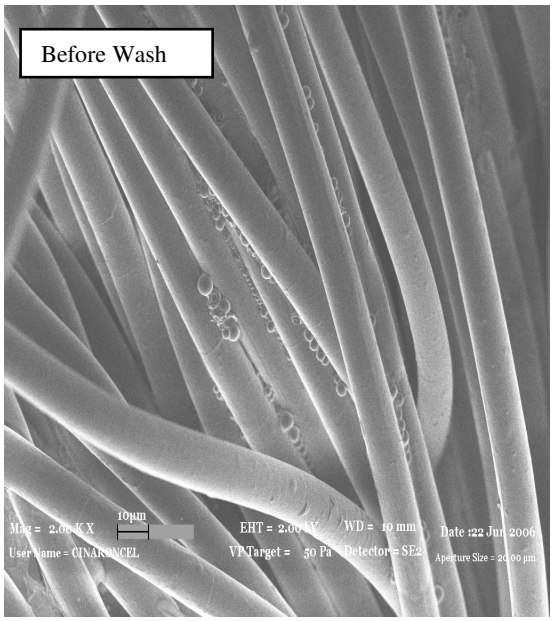
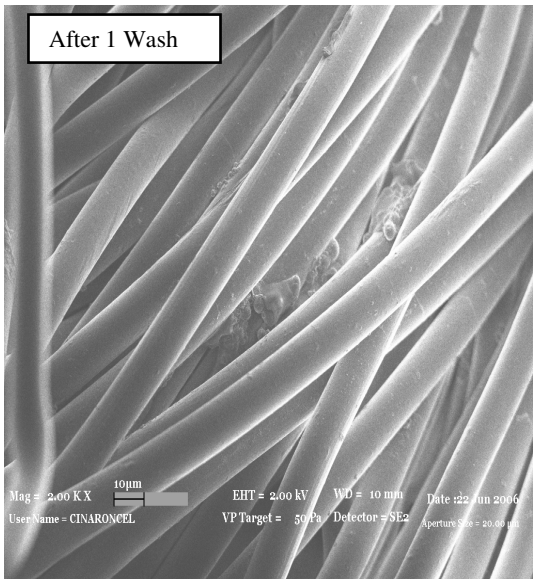


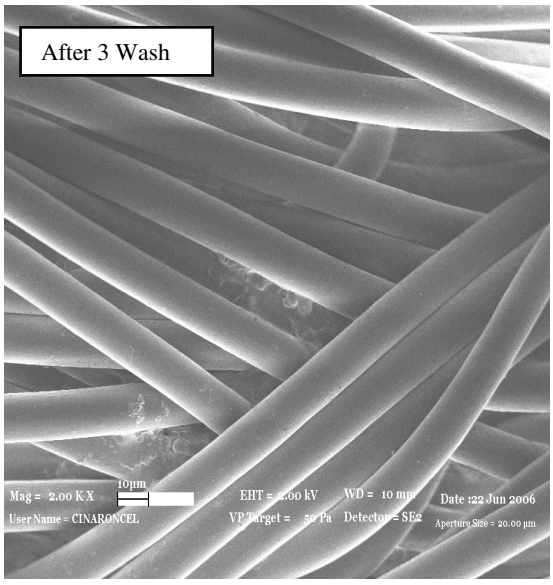
Fig. 4.19: Recipe 8. Foulard Process

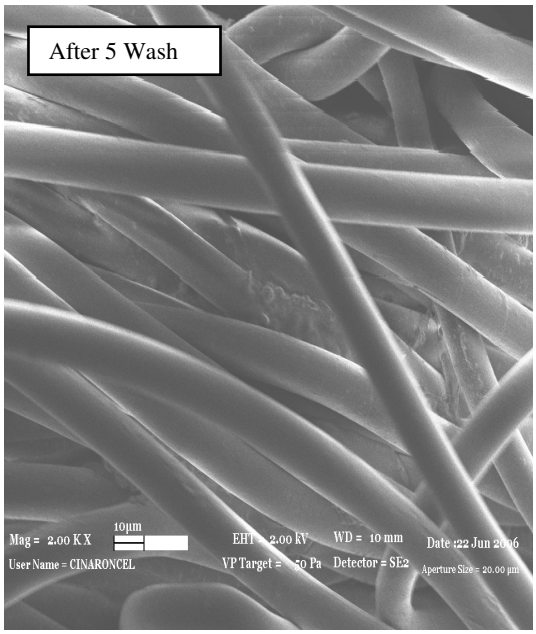
Fig. 4.19 shows the result of Recipe 8. Before wash on the fabric, it is seen a lot of microcapsules on the yarn. But after 1 wash cycle, most of the microcapsules are disappeared. This confirm us binder 3003A is not a suitable binder for high laundery efficiency.

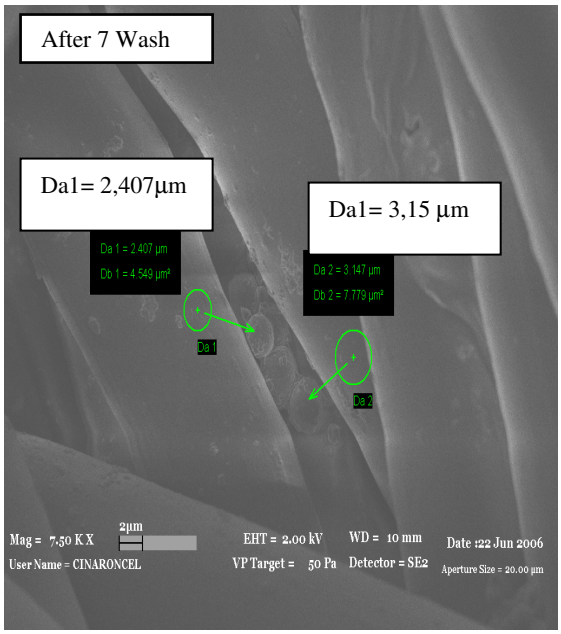

Before Wash
Recipe 9
Foulard Method
Da1= 4,86µm
Da1= 2,58µm


Before Wash


After 1 Wash


After 3 Wash


After 5 Wash


After 7 Wash
Da1= 2,407µm
Da1= 3,15 µm

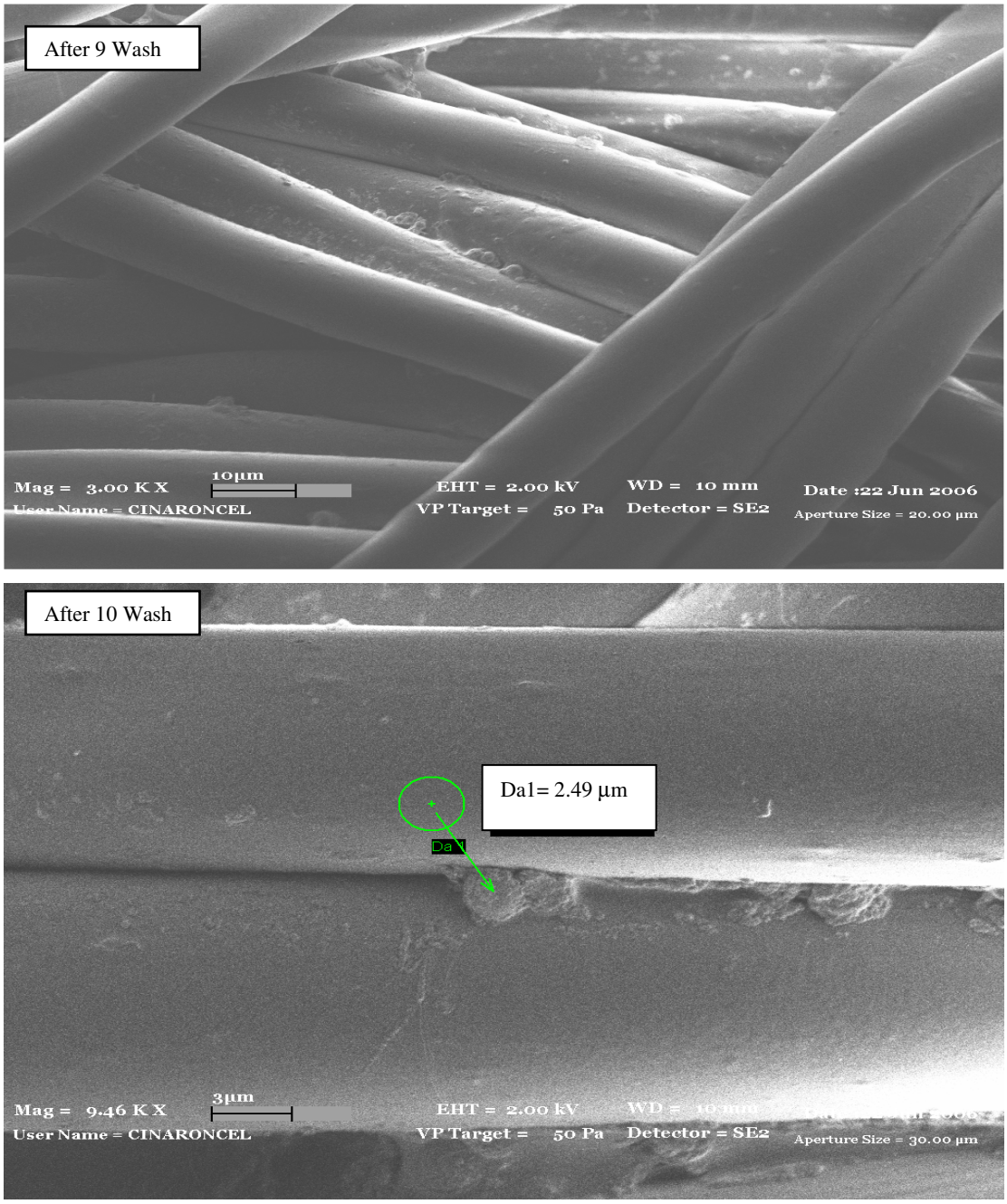


Fig. 4.20: Recipe 9. Foulard Process

Fig. 4.20 shows us the results of Recipe 9. It is seen that there are a lot of microcapsules on the yarn before washing. After 9th and 10th wash cycles there are still microcapsules bounded on yarn, however, the spherical shape of the capsules are slightly changed after 10 washes. Recipe 9 has the same microcapsule size with Recipe 7 and Recipe 8, but when we compare Fig 4.18, 4.19 and 4.20, it can be concluded that the binder quality has an important influence on the microcapsule release amount. Binding efficiency of binder 3009A is found moderate while 3001A+3002A is the best and 3003A is the worst. If we compare the photographs of

Recipe 1, Recipe 4 and Recipe 7 that have the same binders (3001A+3002A) but different capsule sizes (A, B and C) on Fig 4.12, 4.15 and 4.18, it can be seen that there are more microcapsules with Recipe 7 and Recipe 1 than Recipe 4. This result is also confirmed with the lost index results by gas chromatography. This might be explained with the better coverage of smaller size of capsules by the same binders.

4.3. Laundering durability evaluation of chitosan coated fabric

Table 4.5 shows the results of gas chromatographic analyses of vitamin E in microencapsulated fabric by foulard method for three selected recipes without chitosan application. Table 4.6 shows the results of gas chromatographic analyses of vitamin E microencapsulated fabric by foulard method for three selected recipes with chitosan application.

Table 4.5: Gas-chromatographic Analysis of Vitamin E in Microencapsulated Fabric by Foulard Process

Recipe Type (Without Chitosan)	**Vitamin E Average Weight % (w/w)**	**Release Amount By Weight % (w/w)**	**Lost Index After 10 Washes**
Recipe C1 without Chitosan - capsule A - before wash	0,127		1,000
Recipe C1 without Chitosan - capsule A - 1 wash	0,129	0,020	1,016
Recipe C1 without Chitosan - capsule A - 5 wash	0,078	0,051	0,614
Recipe C1 without Chitosan - capsule A - 10 wash	0,073	0,005	0,575
Vitamin E Amount% decrease between before and after 10 wash	42,5%		
Recipe C4 without Chitosan - capsule B - before wash	0,196		1,000
Recipe C4 without Chitosan - capsule B - 1 wash	0,174	0,022	0,888
Recipe C4 without Chitosan - capsule B - 5 wash	0,096	0,078	0,490
Recipe C4 without Chitosan - capsule B - 10 wash	0,092	0,006	0,469
Vitamin E Amount% decrease between before and after 10 wash	53,1%		
Recipe C7 without Chitosan - capsule C - before wash	0,200		1,000
Recipe C7 without Chitosan - capsule C - 1 wash	0,207	+ 0,007	1,035
Recipe C7 without Chitosan - capsule C - 5 wash	0,151	0,056	0,755
Recipe C7 with**out** Chitosan - capsule C - 10 wash	0,146	0,005	0,730
Vitamin E Amount% decrease between before and after 10 wash	27,0%		

Table 4.7 shows the results of gas chromatographic analyses of myritol 318 coconut oil in microencapsulated fabric by foulard method for three selected recipes without chitosan application. Table 4.8 shows the results of gas chromatographic analyses of myritol 318 coconut oil microencapsulated fabric by foulard method for three selected recipes with chitosan application.

On Table 4.5, it can be followed the microcapsule decrease amount after first, fifth and 10^{th} wash cycles. It is seen that there is not a big loss after first wash but after

five washes there is a considerable loss of microcapsules and after ten washes, there is not a big difference between the amounts of microcapsules on the fabrics when compared with 5th wash results.

Table 4.6: Gas-chromatographic Analysis of Vitamin E in Chitosan Coated Microencapsulated Fabric by Foulard Process

Recipe Type (With Chitosan)	**Vitamin E Average Weight % (w/w)**	**Release Amount By Weight % (w/w)**	**Lost Index After 10 Washes**
Recipe CI with Chitosan capsule A - before wash	0,124		1,000
Recipe CI with Chitosan capsule A - 1 wash	0,122	0,002	0,122
Recipe CI with Chitosan capsule A - 5 wash	0,099	0,023	0.099
Recipe CI with Chitosan capsule A - 10 wash	0,090	0,009	0,090
Vitamin E Amount % decrease between before and after 10 wash	27,4%		
Recipe C4 with Chitosan capsule B - before wash	0,222		1,000
Recipe C4 with Chitosan capsule B - 1 wash	0,223	0	1,005
Recipe C4 with Chitosan capsule B - 5 wash	0,132	0,091	0,595
Recipe C4 with Chitosan capsule B - 10 wash	0,126	0,006	0,568
Vitamin E Amount % decrease between before and after 10 wash	43,2%		
Recipe C7 with Chitosan capsule C - before wash	0,171		1,000
Recipe C7 with Chitosan capsule C - 1 wash	0,159	0,012	0,927
Recipe C7 with Chitosan capsule C - 5 wash	0,125	0,034	0,729
Recipe C7 with Chitosan capsule C - 10 wash	0,111	0,014	0,650
Vitamin E Amount% decrease between before and after 10 wash	35,1%		

Table 4.7: Gas-chromatographic Analysis of Myritol 318 in Microencapsulated Fabric by Foulard Process

Recipe Type (Without Chitosan)	**Myritol 318 Average Weight % (w/w)**	**Release Amount By Weight % (w/w)**	**Lost Index After 10 Washes**
Recipe CI without Chitosan - capsule A - before wash	1,290		1,000
Recipe CI without Chitosan - capsule A - 1 wash	1,260	0,030	0,977
Recipe CI without Chitosan - capsule A - 5 wash	0,762	0,498	0,591
Recipe CI without Chitosan - capsule A -10 wash	0,727	0,035	0,564
Myritol 318 Amount % decrease between before and after 10 wash	43,6%		
Recipe C4 without Chitosan - capsule B - before wash	1,700		1,000
Recipe C4 without Chitosan - capsule B - 1 wash	1,330	0,370	0,782
Recipe C4 without Chitosan - capsule B - 5 wash	0,775	0,555	0,456
Recipe C4 without Chitosan - capsule B - 10 wash	0,715	0,060	0,421
Myritol 318 Amount % decrease between before and after 10 wash	57,9%		
Recipe C7 without Chitosan - capsule C - before wash	1,640		1,000
Recipe C7 without Chitosan - capsule C - 1 wash	1,650	0,01	1,006
Recipe C7 without Chitosan - capsule C - 5 wash	1,180	0,470	0,720
Recipe C7 without Chitosan- capsule C - 10 wash	1,110	0,007	0,677
Myritol 318 Amount % decrease between before and after 10 wash	32,3%		

Myritol 318 coconut oil results are also similar with Vitamin E. It is seen on Table 4.7 that the loss of microcapsules is small after first wash and after 5th wash there is a big loss and remains after 10th wash.

After application of chitosan the microcapsule loss amounts decrease but the biggest loss is still after 5 washing cycles comparing the before wash amount.

Table 4.8: Gas-chromatographic Analysis of Myritol 318 in Chitosan Coated Microencapsulated Fabric by Foulard Process

Recipe Type (With Chitosan)	**Myritol 318 Average Weight % (w/w)**	**Release Amount By Weight % (w/w)**	**Lost Index After 10 Washes**
Recipe CI with Chitosan capsule A - before wash	1,240		1,000
Recipe CI with Chitosan capsule A - 1 wash	1,170	0,070	0,944
Recipe CI with Chitosan capsule A - 5 wash	1,040	0,130	0,839
Recipe CI with Chitosan capsule A - 10 wash	0,993	0,0470	0,801
Myritol 318 Amount % decrease between before and after 10 wash	19,9%		
Recipe C4 with Chitosan capsule B - before wash	1,580		1,000
Recipe C4 with Chitosan capsule B - 1 wash	1,440	0,140	0,911
Recipe C4 with Chitosan capsule B - 5 wash	1,310	0,130	0,829
Recipe C4 with Chitosan capsule B - 10 wash	1,340	0,030	0,848
Myritol 318 Amount % decrease between before and after 10 wash	15,2%		
Recipe C7 with Chitosan capsule C - before wash	1,310		1,000
Recipe C7 with Chitosan capsule C - 1 wash	1,200	0,110	0,916
Recipe C7 with Chitosan capsule C - 5 wash	1,160	0,040	0,885
Recipe C7 with Chitosan capsule C - 10 wash	1,060	0,100	0,809
Myritol 318 Amount % decrease between before and after 10 wash	19,1%		

In the study of Kyeyoun C, et al [141], a 100% polyester fabric was chosen as the specimen for microcapsule treatment via coating method. And as active ingredient inside of the capsule, a phase change material, octadecane, was used. In their study, thermal storage and release properties of this microcapsule treated fabric was examined at the repeated laundering stages, similar to this thesis, before washing, after 1 wash, after 5 wash and after 10 wash. In their study, they found out that the biggest decrease occurred after the first laundering, and small decreases occurred after five launderings. It appears that, unavoidably, capsules fall of the fabric because of friction during repeated launderings. The SEM results before and after launderings show that the surface of the fabric before laundering is fully covered with the coating mixture, but the coating after launderings has peeled off and there are sparsely bonded coating materials in the intersections of the polyester yarn.

However, our study, the biggest capsule lost was not seen after the first laundering, it was seen after 5 washing cycles. Moreover, if we compare the release rate of Table

2.19 and Table 4.7 – 4.8 with each other, it is seen that the release rate in this thesis is improved a lot for the 1st, 5th and 10th laundering cycles than that of the study of Kyeyoun C, et al [141].

A much visible improvement on release rate was seen in gas chromatographic results after the chitosan solution coating onto the already microcapsule treated fabric beforehand. (Table 4.6-Table 4.8). Before washing, after one wash, five times wash and ten times wash result by gas chromatography for both vitamin E and myritol 318 coconut oil were recorded in both "with" and "without" chitosan coating on microencapsulated fabric.

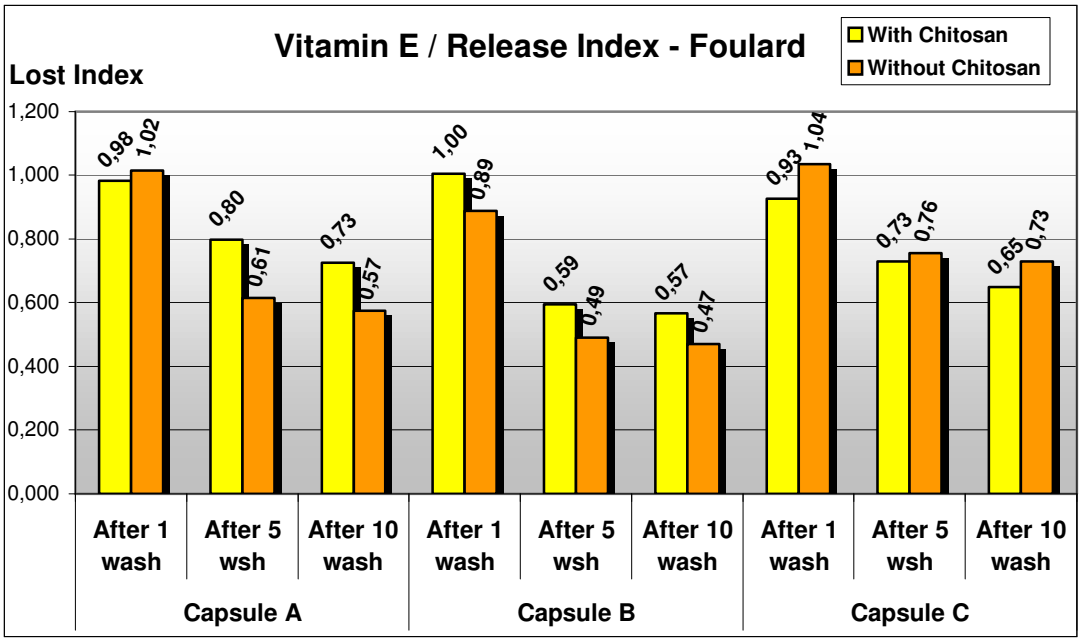


Fig. 4.21: Vitamin E Lost Index in Foulard Process for Both "with" and "without" Chitosan Coating on Microencapsulated Fabric by Capsule A, B and C.

When both "with" chitosan and "without" chitosan results were transformed in to the release rate index in (Fig. 4.21 and 4.22) for a clear comparison, the improvement was seen clearly in the graphics. In both vitamin E and Myritol 318 oil's release rate for the "chitosan coated" microencapsulated fabric is between 10 % (Fig. 4.21) and 42,8 % (Fig.4.22) better than that of just microencapsulated fabric. So, this result shows that chitosan can be used to enhance the laundering performance of microencapsulated textile materials. The only unexpected result was in Recipe C7 with capsule C: the lost index of Vitamin E was seen much better "without chitosan" than "with chitosan".

The benefits of chitosan also stated by various researchers [34, 35, 78,118, 123] that it has been always a very useful and key natural polymer in microcapsule manufacturing methods. Chitosan has been used as one of the shell polymer of the microcapsules in different industries.

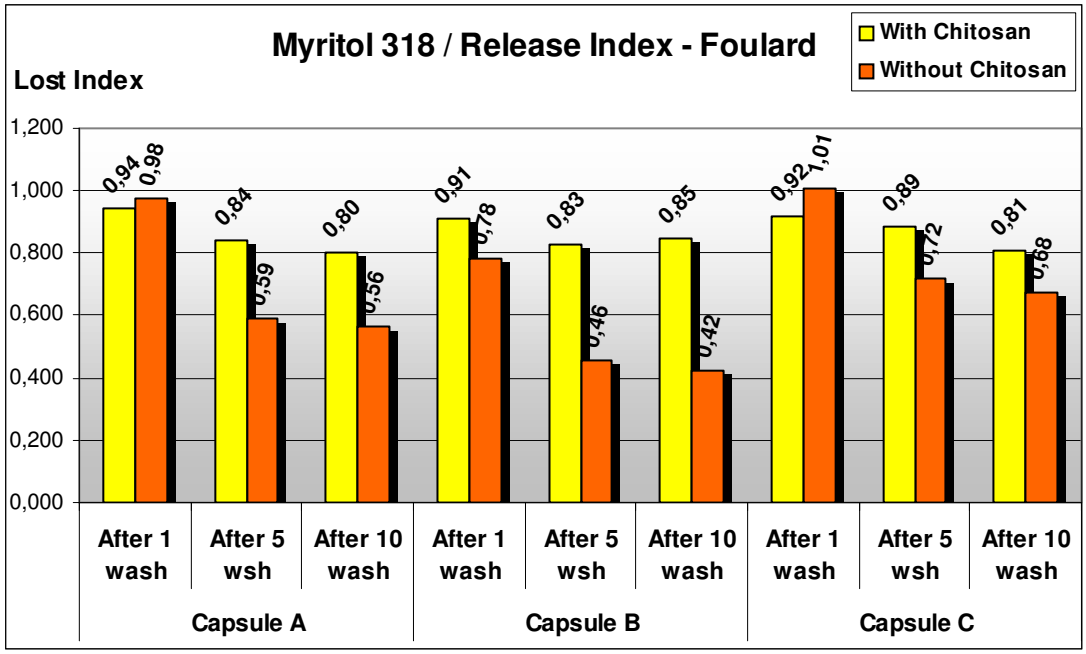


Fig. 4.22: Myritol 318 Coconut Oil Lost Index in Foulard Process for Both "with" and "without" Chitosan Coating on Microencapsulated Fabric by Capsule A, B and C.

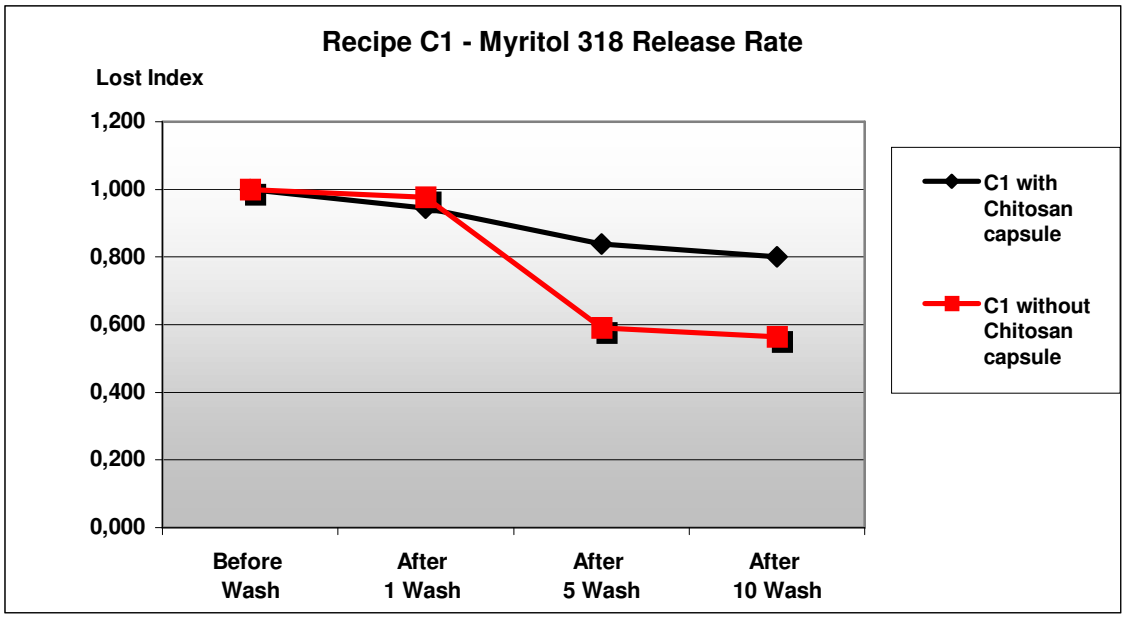


Fig. 4.23: Myritol 318 Oil Lost Index Comparison for Both "with chitosan" and "without chitosan" Treated Fabric in Recipe C1.

In Fig 4.23 it is clearly seen that there is about 23,7 % Myritol 318 oil release rate improvement between "with chitosan" and "without chitosan" used microencapsulated fabric.

In Fig 4.24 it is clearly seen that there is about 42,8 % Myritol 318 oil release rate improvement between "with chitosan" and "without chitosan" used microencapsulated fabric.

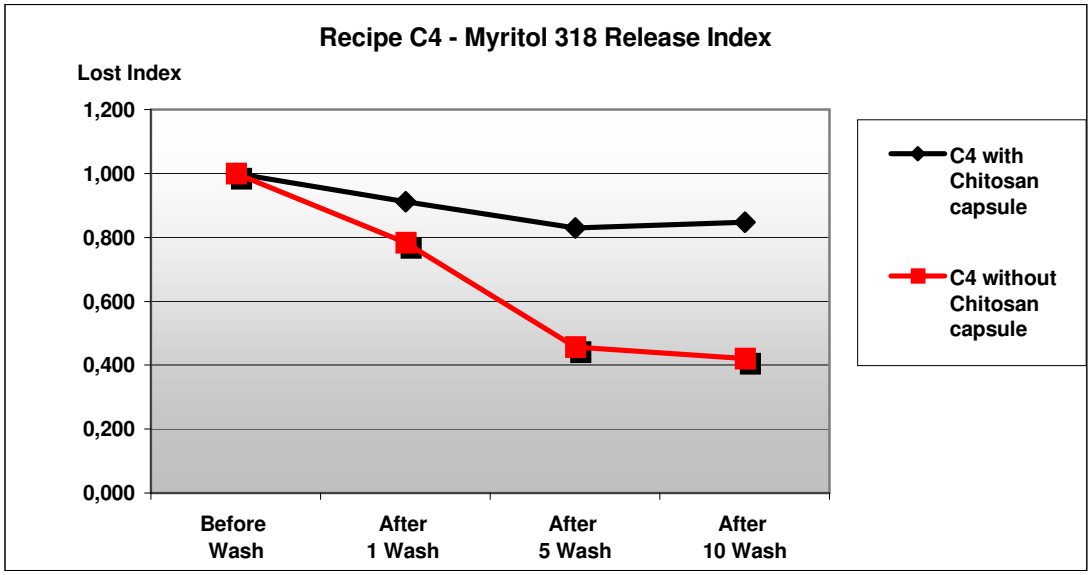


Fig. 4.24: Myritol 318 Oil Lost Index Comparison for Both "with Chitosan" and "without Chitosan" Treated Fabric in Recipe C4.

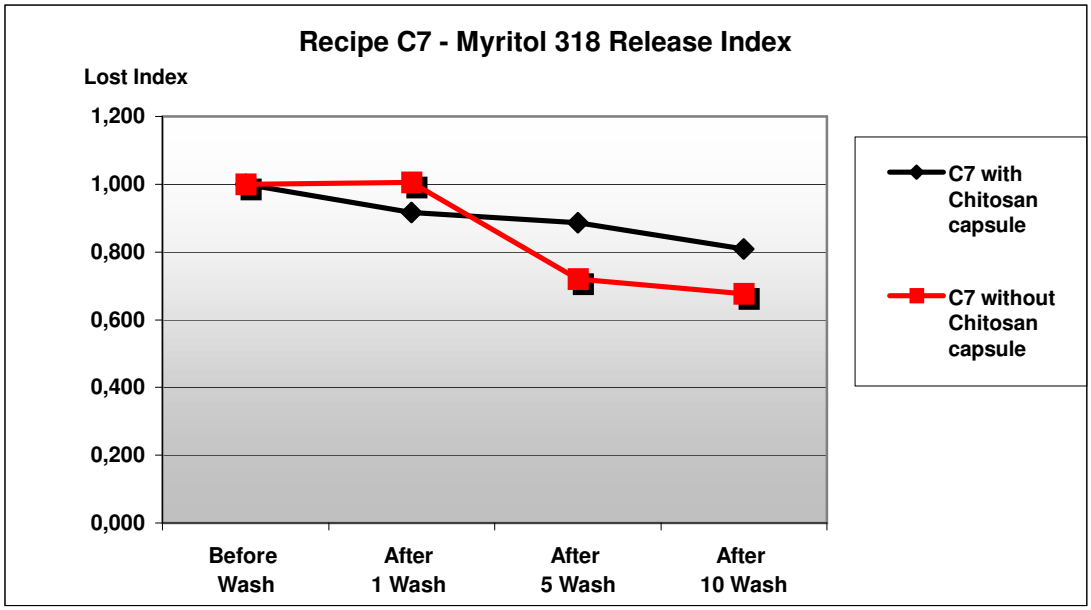


Fig. 4.25: Myritol 318 Oil Lost Index Comparison for Both "with Chitosan" and "without Chitosan" Treated Fabric in Recipe C7.

In Fig 4.25 it is clearly seen that there is about 13,2 % Myritol 318 oil release rate improvement between "with chitosan" and "without chitosan" used microencapsulated fabric.

In this thesis, rather than using chitosan as a shell polymer of the microcapsules, in different direction, it was used as a kind of coating material via secondary foulard

process by applying on to the already microcapsule treated fabric. It is concluded that chitosan made a natural coating blanket onto the microcapsules and helped microcapsules to increase their resistance against any wet processes in further.

To prove the improvement on the laundering durability resistance of the chitosan coated microcapsule treated fabric, gas-chromatographic analyses as well as scanning electron-microscopic analyses were made for both "with" and "without" chitosan coating on microencapsulated fabric. (Table 3.7) (Recipe 1C, Recipe 4C and Recipe 7C).

In the research of Wen-Chuan H, Chih-Pong C, Ying-Lin G in 2006 [118], it was stated that the thicker the chitosan concentration, the slower the release rate of volatile citronella oil. This is because the higher the chitosan concentration, the thicker the microcapsules wall membrane and smaller the pore space between chitosan molecules, therefore causes difficulties for the volatile citronella oil release from microcapsules (Fig.2.60). They were stated that the higher the operation environment temperatures, the longer the release time. And they pointed that 80° C was giving better result than that of 40 °C and 60 °C. Yet if the operation environment temperature were increased to 80 °C, the microcapsule encapsulated Citronella Oil has initial low release rate, and declining to nearly none when operation time is close to 50 min. The reason is that the chitosan molecule chains gradually contract because the microcapsule wall membrane was heated; intermolecular space is then reduced; therefore slow down the Citronella Oil release rate gradually. So along with the operation time increase, the wall membrane structure highly contracted causing the pores nearly completely seal off and the volatile Citronella Oil unable to continue to release.

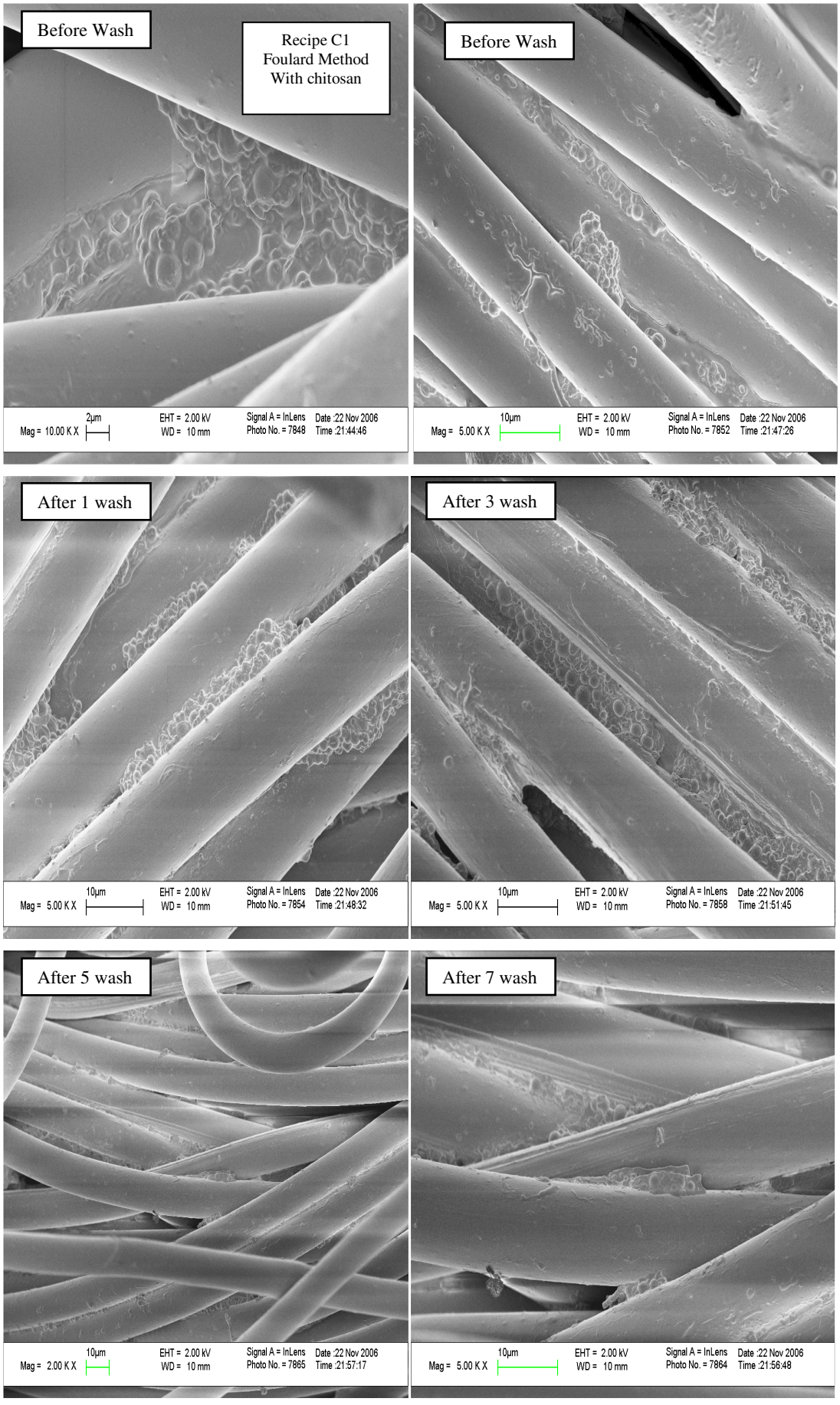
The microcapsule treated fabric that is applied by foulard process, with recipes listed in Table 3.7, was also alternatively post- treated with chitosan/ lactic acid solution (3% Chitosan, 1.6% lactic acid) in a secondary foulard process and then the curing was made under 120 °C during 3 minutes in Mathis Dryer. So, this temperature should be more than enough for shrinking the chitosan pore. In the study of Wen-Chuan H, et al, in 2006 [118], it was mentioned that at the 80 °C, the pores of chitosan was almost closed when the process time extended to 50 minutes. In this thesis, just 3 minutes drying time was taken so as not to give any damage to the fabric properties as well as to the release rate index of fabric. On the other hand, 120

°C curing temperature during 3 minutes should have helped enough for the shrink of the chitosan pores.

Similar to the study of Wen-Chuan H, Chih-Pong C, Ying-Lin G in 2006 [118], in the study of Ye, S., et al [124], they also mentioned that more chitosan means, relatively more compact surface structure; more surface structure helps strengthening of the capsule resistance.

So, this is also a significant reason why chitosan solution was added into the secondary foulard bath in this thesis. It was thought that chitosan solution would make an additional wall surface, like a blanket, onto the already microencapsulated fabric, and during the curing process, which is 120 °C during 3 minutes in Mathis Dryer (Table 4.3.1), this chitosan blanket pores will get shrunk and the release tendency of the vitamin E and myritol oil will get decreased similar to the Citronella Oil mentioned in Wen-Chuan H, Chih-Pong C, Ying-Lin G in 2006 [118], because an additional wall membrane will be added around the capsule wall.

In the study of Shiqu Ye, Chaoyang Wang, Xinxing Liu, Zhen Tong, Beye Ren and Fang Zeng [124], they stated that any increase on the number of the membrane layers slow down the insulin release speed, because the additional deposited layers on the loaded microcapsules will give rise to an extra barrier to the insulin molecule movement, thus slow down the release rate. Again, one of the other inspirations of this thesis was the study of Shiqu Ye, Chaoyang Wang, Xinxing Liu, Zhen Tong, Beye Ren and Fang Zeng [124]. To increase the number of the membrane layers around the microcapsules, additional chitosan solution was used in the secondary foulard process as secondary coating membrane wall. The results showed that this additional layer helped to retard the release of vitamin E and myritol oil as seen in Fig. 4.23, Fig. 4.24 and Fig. 4.25 and in gas- chromatographic analyses results (Table 4.5- Table 4.8).


Before Wash
Recipe C1
Foulard Method
With chitosan
2µm
Mag = 10.00 K X
EHT = 2.00 kV
WD = 10 mm
Signal A = InLens
Photo No. = 7848
Date :22 Nov 2006
Time :21:44:46
Before Wash
10µm
Mag = 5.00 K X
EHT = 2.00 kV
WD = 10 mm
Signal A = InLens
Photo No. = 7852
Date :22 Nov 2006
Time :21:47:26
After 1 wash
10µm
Mag = 5.00 K X
EHT = 2.00 kV
WD = 10 mm
Signal A = InLens
Photo No. = 7854
Date :22 Nov 2006
Time :21:48:32
After 3 wash
10µm
Mag = 5.00 K X
EHT = 2.00 kV
WD = 10 mm
Signal A = InLens
Photo No. = 7858
Date :22 Nov 2006
Time :21:51:45
After 5 wash
10µm
Mag = 2.00 K X
EHT = 2.00 kV
WD = 10 mm
Signal A = InLens
Photo No. = 7865
Date :22 Nov 2006
Time :21:57:17
After 7 wash
10µm
Mag = 5.00 K X
EHT = 2.00 kV
WD = 10 mm
Signal A = InLens
Photo No. = 7864
Date :22 Nov 2006
Time :21:56:48

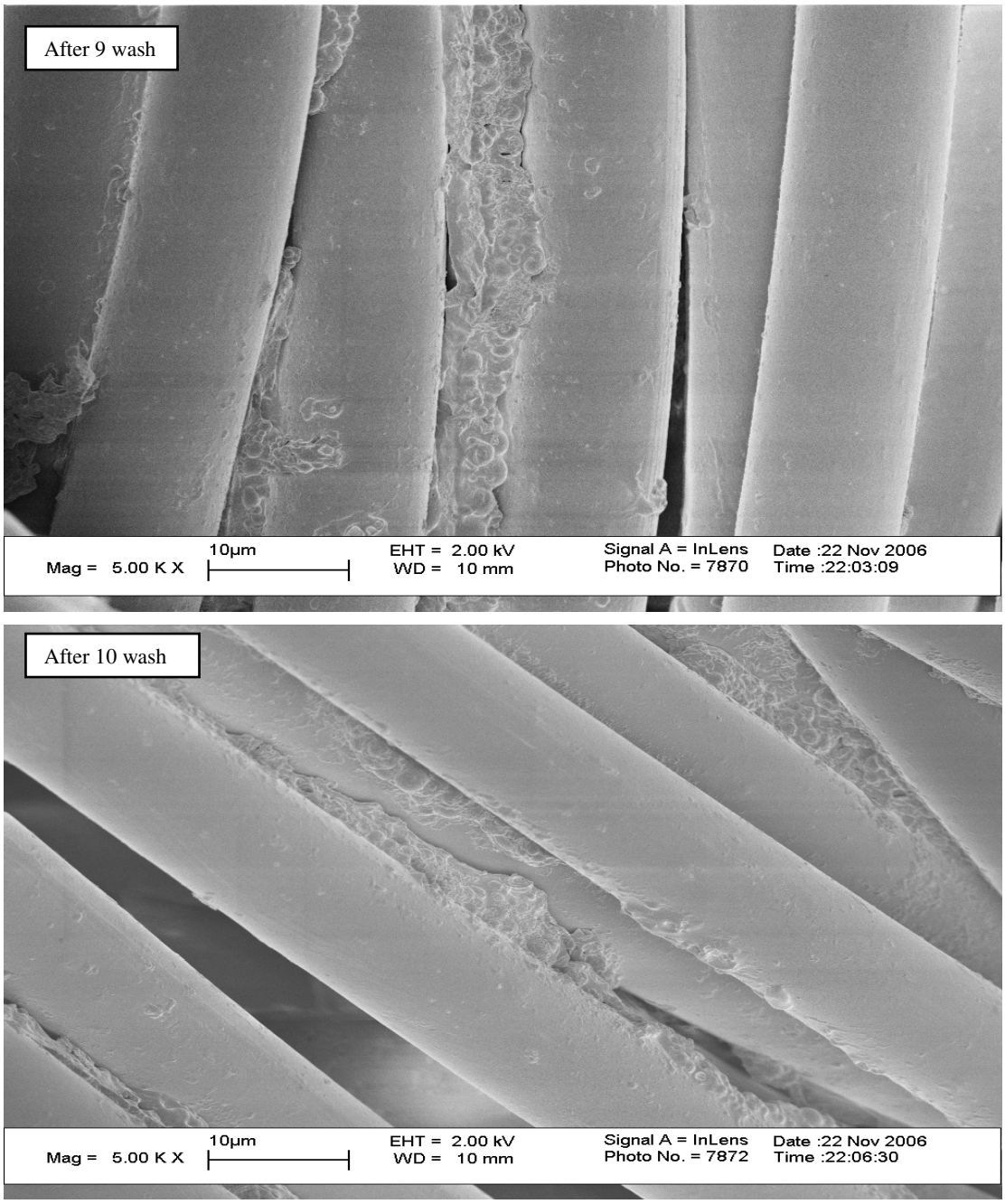
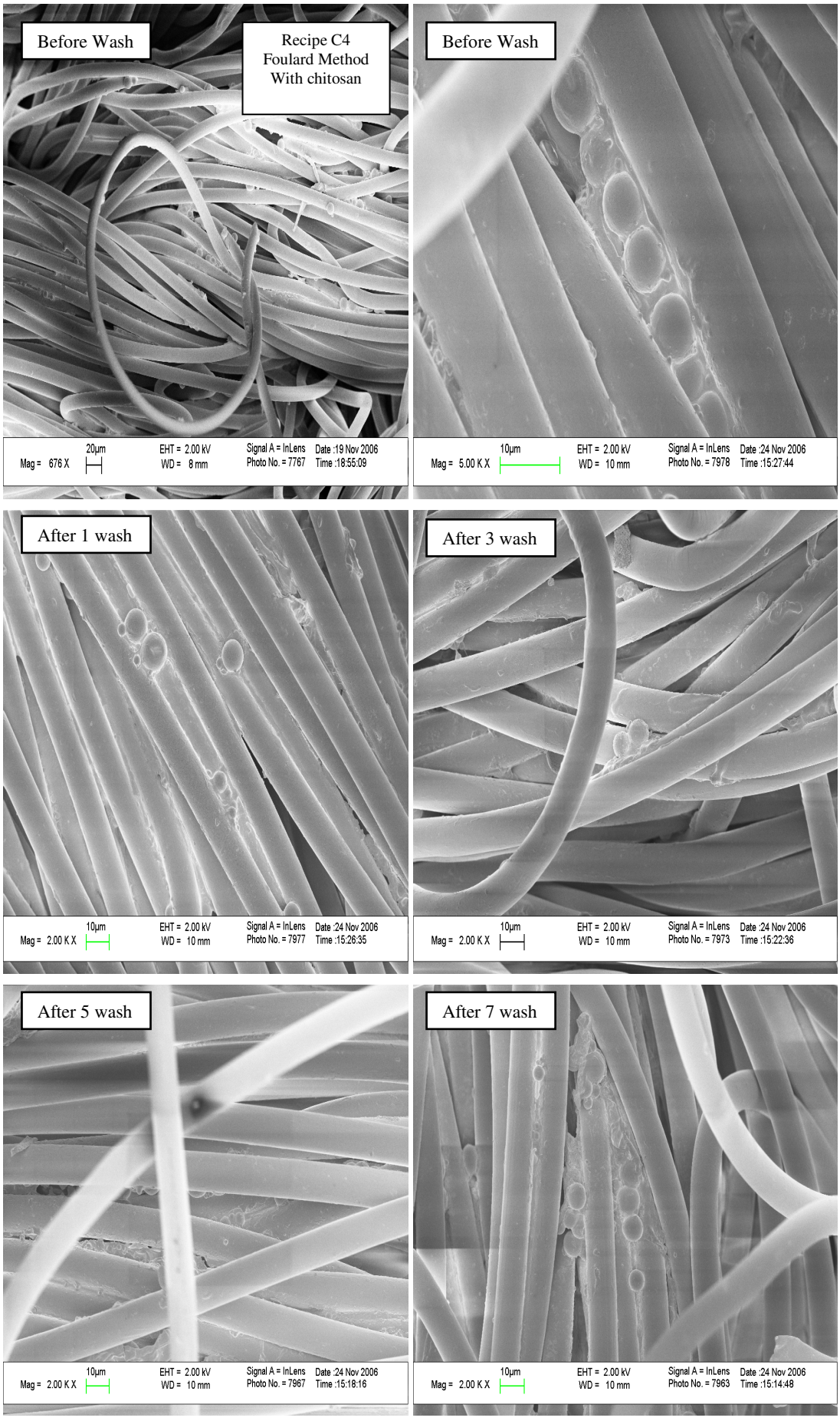


Fig. 4.26: Recipe 1C with Chitosan Coating Via Secondary Foulard Process

Fig. 4.26 shows the chitosan-applied sample with Recipe C1. It is seen that there are not big losses after first and third wash, but after fifth wash the loss of microcapsules can be seen easily, but after ten wash cycles there are still big amount of microcapsules on the yarns.


Before Wash
Recipe C4
Foulard Method
With chitosan
Mag = 676 X
20µm
EHT = 2.00 kV
WD = 8 mm
Signal A = InLens
Photo No. = 7767
Date :19 Nov 2006
Time :18:55:09
Before Wash
Mag = 5.00 K X
10µm
EHT = 2.00 kV
WD = 10 mm
Signal A = InLens
Photo No. = 7978
Date :24 Nov 2006
Time :15:27:44
After 1 wash
Mag = 2.00 K X
10µm
EHT = 2.00 kV
WD = 10 mm
Signal A = InLens
Photo No. = 7977
Date :24 Nov 2006
Time :15:26:35
After 3 wash
Mag = 2.00 K X
10µm
EHT = 2.00 kV
WD = 10 mm
Signal A = InLens
Photo No. = 7973
Date :24 Nov 2006
Time :15:22:36
After 5 wash
Mag = 2.00 K X
10µm
EHT = 2.00 kV
WD = 10 mm
Signal A = InLens
Photo No. = 7967
Date :24 Nov 2006
Time :15:18:16
After 7 wash
Mag = 2.00 K X
10µm
EHT = 2.00 kV
WD = 10 mm
Signal A = InLens
Photo No. = 7963
Date :24 Nov 2006
Time :15:14:48

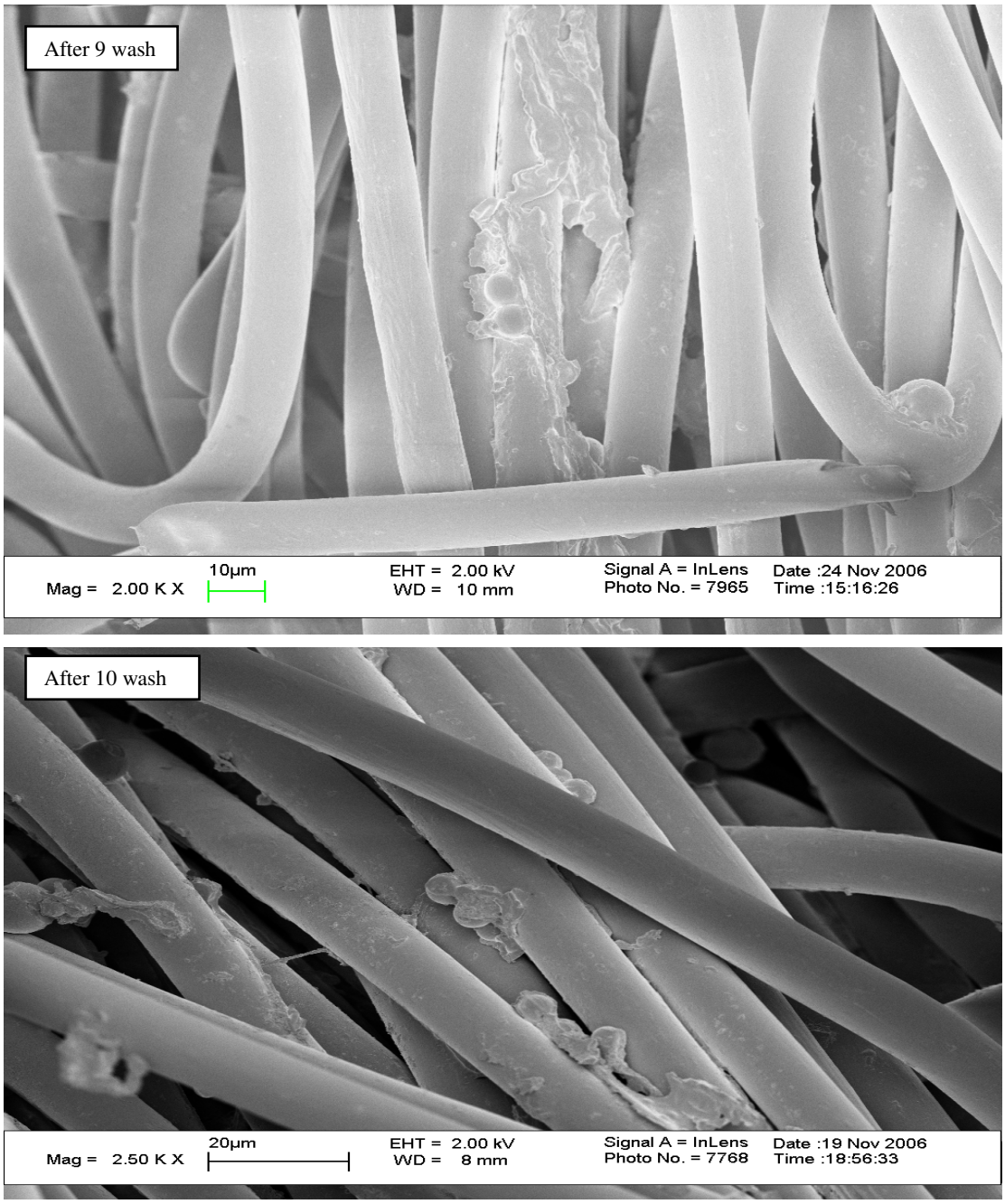
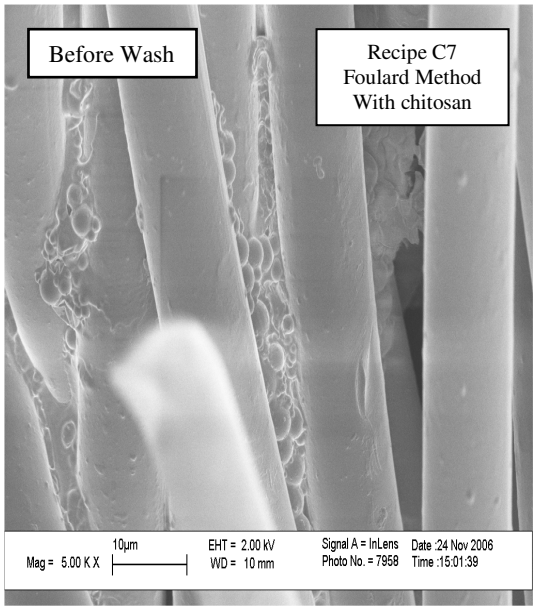
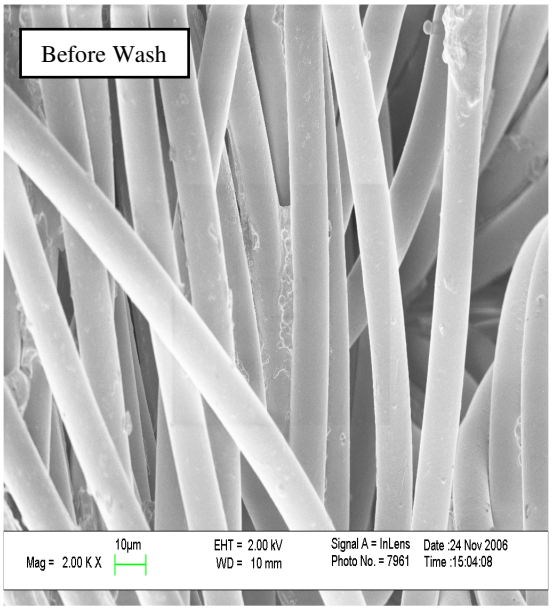
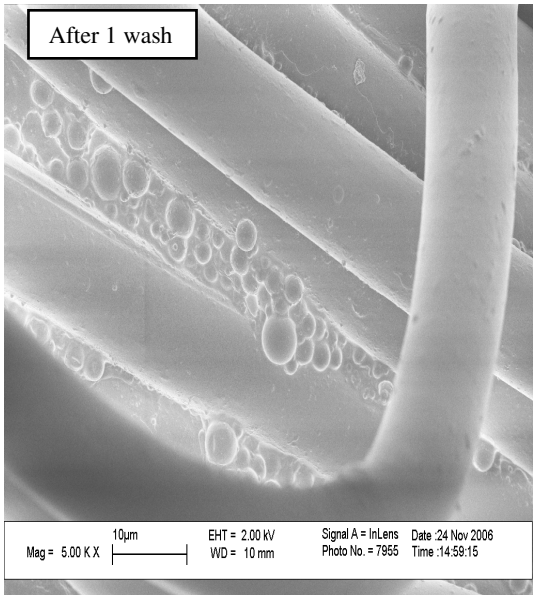


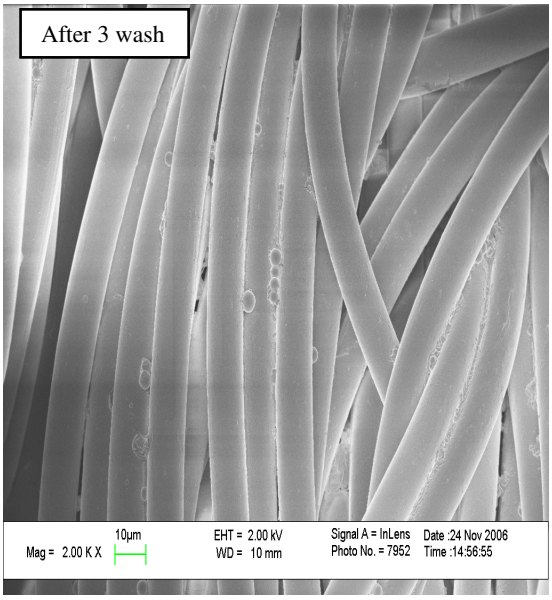
Fig. 4.27: Recipe 4C with Chitosan Coating Via Secondary Foulard Process

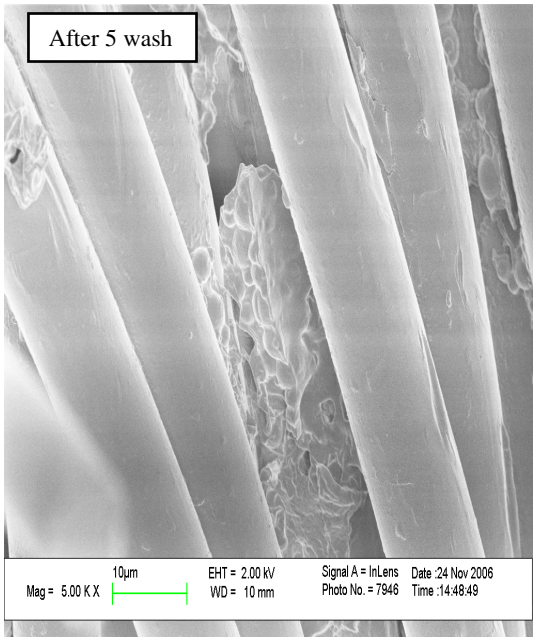
Fig 4.27 shows the chitosan applied sample with Recipe C4. It is seen the spherical shapes of microcapsules before wash, after first wash and after third wash; after fifth wash the shape begins to change and after 10^{th} wash cycle it is seen that nearly half of the capsules are damaged, but still bounded to the yarn.

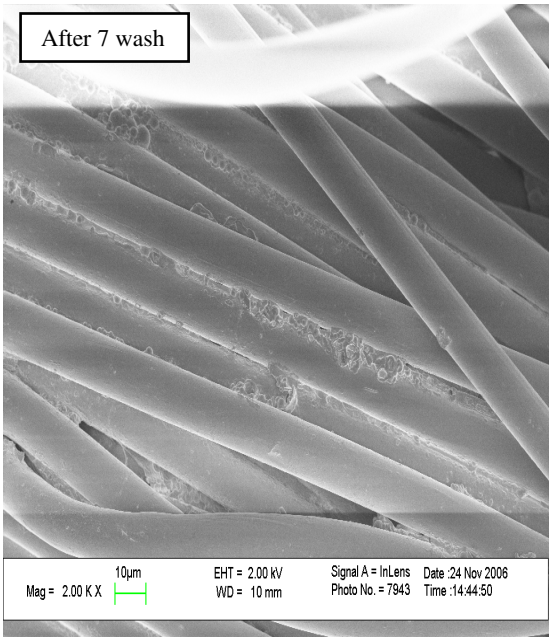

Before Wash
Recipe C7
Foulard Method
With chitosan
10µm
Mag = 5.00 K X
EHT = 2.00 kV
WD = 10 mm
Signal A = InLens
Photo No. = 7958
Date :24 Nov 2006
Time :15:01:39


Before Wash
10µm
Mag = 2.00 K X
EHT = 2.00 kV
WD = 10 mm
Signal A = InLens
Photo No. = 7961
Date :24 Nov 2006
Time :15:04:08


After 1 wash
10µm
Mag = 5.00 K X
EHT = 2.00 kV
WD = 10 mm
Signal A = InLens
Photo No. = 7955
Date :24 Nov 2006
Time :14:59:15


After 3 wash
10µm
Mag = 2.00 K X
EHT = 2.00 kV
WD = 10 mm
Signal A = InLens
Photo No. = 7952
Date :24 Nov 2006
Time :14:56:55


After 5 wash
10µm
Mag = 5.00 K X
EHT = 2.00 kV
WD = 10 mm
Signal A = InLens
Photo No. = 7946
Date :24 Nov 2006
Time :14:48:49


After 7 wash
10µm
Mag = 2.00 K X
EHT = 2.00 kV
WD = 10 mm
Signal A = InLens
Photo No. = 7943
Date :24 Nov 2006
Time :14:44:50

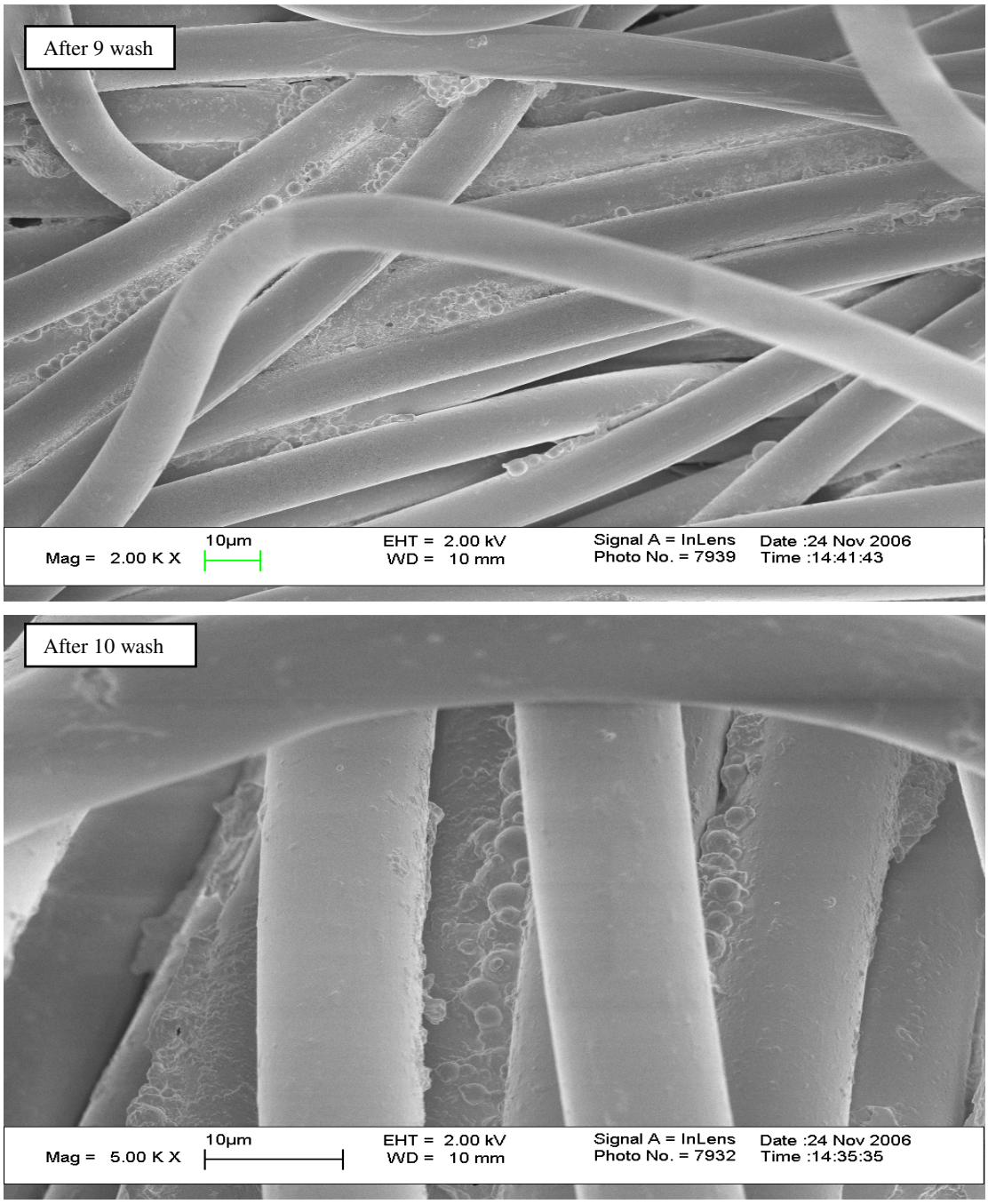


Fig.4.28: Recipe 7C with Chitosan Coating Via Secondary Foulard Process

Fig. 4.28 shows the chitosan-applied sample with Recipe 7. The results are quite similar with Recipe C1 and Recipe C4. All above results found in this thesis and all previous researches are clearly supporting the usage of chitosan for textile industry to have a better laundering durability performance in the area of microencapsulation technology.

4.4. Conclusion and Suggestions

As a result of this study, smaller capsules will normally be bound stronger to the textile because they are more "immerged" in the binder. On the other hand their shell is less thick in absolute terms so that losses of content because of unexpected diffusion are easier. Larger capsules should be easier to abrade away in wash processes but since their shell is thicker, they should lose less against unexpected diffusion formation and they should be stronger than that of smaller ones against any environmental conditions [217]. Therefore, to have a clear judgment on the choice of the most proper capsule size in terms of having the best laundering durability, further studies are crucially necessary. In this study, it is seen that binder quality has the prior importance than the size of the capsules

This study also proved us that chitosan coating process had a real positive effect to improve the release rate of Vitamin E and Myritol 318 coconut oil for the prepared microcapsules in all three different sizes.

The other important parameter is to use suitable binder quality, which does not affect the handle in a negative way. It was found out that the binder quality has to have hydrophobic properties so that in further end consumer washings are not affecting the resistance of the capsules against water. In this study, binder 3001A and binder 3002A combination was the best performer due to its hydrophobic properties and its strong adhesive characteristic. Also 3009A gave a good laundering durability result, since it is a quite strong binder and has also hydrophobic properties similar to 3001A and 3002A combination binder. 3003A due to its hydrophilic character is found not suitable for microcapsule applications.

The differences between foulard, exhaust and coating process in the application of microcapsules:

Foulard offers a forced application of actives onto the textile, therefore a more controlled loading of the textile. By the calculation of bath concentration and wet pick up we can determine the loading of the textile. Exhaustion is an "uncontrolled" process, where the active ingredients are applied. The control mechanism is less basically only the turbidity of the remaining bath. Second benefit is with foulard the

choice of binders is more wide range, again the controlled pick up of binder and better curing possibilities and after foulard typically a stenter frame follows.

Foulard application is always the best, because it is easy and reliable and the transfer to the fabric is 100% contrary to exhaust application.

There are not many good binders, which can be exhausted. This is an important reason why the wash durability is often less good after exhaust application.

Exhaust application is only used when there is no other choice like on jeans or on pantyhose. Hence, for finished garments, exhaust method can be a good alternative to foulard one [218].

Basically microcapsules can also be applied by coating. A calendering process afterwards however may destroy a part of the capsules, depending on capsule content, temperature and pressure of the calendering. Secondly, if the capsules are massively coated with a thick layer of polymers, then the release of the ingredient would be much difficult than that of foulard one and the activation of the active ingredient would not be effective. Also, when a polyurethane coating is applied, the type of the polyurethane has to be compatible with the microcapsules, i.e. in consideration with the microcapsules used in this thesis; polyurethane should be also anionic, not cationic. Microcapsules smaller than 1 μm are broken during the coating process due to low stability to solvent [141,161]. So, there is bottom size limit for the coating method in microcapsule applications.

It was found out that the fabric handle worsens with microcapsule coating process in KOR (knife over roll) method. That's why to make the handle much softer SP (screen printing) method was used [141].

Beside exhaust, foulard and coating; microcapsules can also be applied by spraying or by printing.

The main challenges of the microencapsulation implementation onto the textile materials are to earn the end consumers satisfaction. This could be only achieved by producing a highly qualified product with the application of the most proper process. Highly qualified product has to have:

- The best performing characteristic to reflect its properties to the end consumers in an effective way.

- And should have long-life to keep its properties and continuously make the end consumer to feel its positive effect on their body.

Foulard and exhaust processes are the main processes. However, it should be spread out in a larger scope and other different processes should also be taken into account for the microcapsule treatment onto the textile material such as overall print, garment printing and yarn dyeing processes. Further researches in these areas are extremely needed to take the capsule efficacy under control and to have long-life capsule release rate during each and every end consumer usage. All negative side effect caused by the process itself has to be studied and figured out so that the best recipe and process combination could be chosen similarly made in this thesis.

The main focus of this thesis was to increase the efficacy and the activity time of the microcapsules that contain vitamin E and Myritol 318 coconut oil. By trying to find out the best proper binder quality, process type, microcapsule size and furthermore, by applying additional coating process to strengthen the capsules shells against any wet processes, a remarkable progress was obtained in terms of laundering durability. The latest achievement in this new technology in near future should be to have the equal efficacy of microcapsule treated garment during all wearing times of end consumers. Therefore, further studies to improve the release rate mechanism of the microcapsules within the textile material are crucially needed.

Today's textile industry is in the transition zone between the achievement of significant structural and technological milestones in the last two decades or so on one hand, and the realization of highly focused design production of added value products in the entire of commodities to highly sophisticated products on the other.

One of the strong forces behind the general advancement made in the field of textiles has been the application- driven product and market development that is widely associated with technical textiles. Microencapsulation technology examined in this thesis is definitely one of the key processes, which will increase the value of the garment. The biggest challenge in microencapsulation process onto the textile is to be taken the release rate under control and increase microcapsule resistance against the laundering durability of end consumer. And of course, legal rules in the usage of cosmeto-textile products have to be watched out very close so that all implementations and processes are made according to the law.

In conclusion, microencapsulation technology is one of the most important solution for apparel industry to get back the end consumer interest and having the increment on private spending of the people, which were losted during the last decade.

5. APPENDIX

5.1. The Effects of The EU-Cosmetic Directive on Cosmeto-Textile

"Cosmetic Product" shall mean any substance or preparation intended to be placed in contact with the various external parts of the human body (epidermis, hair system, nails, lips and external genital organs) with a view exclusively or mainly to cleaning them, perfuming them, changing their appearance and/or correcting body odour and/or protecting them or keeping them in good condition.(European Cosmetic-Directive (76/768 EC dated 27 July 1976, last amended as of 19 July 2006) [221].

5.1.1. Legal Consequence of Clothes Being the "Packaging" for Cosmetic Products

Cosmetic products may only be placed on the market if the packaging and the container bear the following in formation in easily legible and visible lettering:

- Address of person being responsible for marketing of cosmetic products
- Date of minimum durability (for those products having a minimum durability of more than 30 months: symbol of opened crème pot)
- Health warnings: if potential allergens may lead to skin reactions
- Batch number of manufacture or the reference for identifying the goods
- Purpose of the product
- List of ingredients in descending order of weight preceded by the word "INGREDIENTS" (INCI)

5.1.2. The Best Way To Label For Legal Requirements

Intention of legal requirements especially, label requirements for cosmetic products: protection of the end consumer. This can be guaranteed by:

- Complete labeling on label, tape or hang tag, which is enclosed or attached to the cosmetic product
- Hint on the hangtag to retain it for future references
- Symbol with open book to be sewed into the jeans/ t-shirts.

The best size/ manner of labeling is: Batch- No., health warnings, and address, INCI-List:

- Indelible form: no self-adhesive labels, which can be detached easily
- Easy legible: character size: (min. 6-points), colour, arrangement of the whole setting (paragraphs, subdivisions, breakdowns, etc.)
- Visible form: no hiding of warnings etc. as well as minimum durability, purpose of use and potential storing conditions.

5.1.3. Address of Person Being Responsible

Address of person being responsible for manufacturing or marketing or importing cosmetic products into the EU (Art 6):

- Intention: contact person for complaints or in case of skin reactions
- Company name, seat of the company; abbreviations are possible provided that the company is identifiable and reachable
- Who has to the obligation to declare: manufacturer of cosmetic product or person puts cosmeto-textile into circulation (brand owner) is unclear legal interpretation.

Pro Manufacturer: he knows the content of the cosmetic product

Pro Brand Owner: he knows, which jeans contain which batch of cosmetic product and is able to contact manufacturer without problems and delays.

5.1.4. Date of Minimum Durability

Such indications have to be made for the following cosmetic products:

- Cosmetic products with a minimum durability of less than 30 months (e.g. “shell life: at least until 31 December 2007”)
- Cosmetic products with a minimum durability of more than 30 months: indication of shell life by symbol: (opened crème pot with indication of term (years, months, weeks)

Problem: What is the shelf life of cosmetic products once they are applied onto textiles?

- Depending on kind of application, heat, production process, on additional products (bleaching, coloring agents etc.), on storing conditions (unintended opening of capsules), treatment of the customer (washing, ironing etc.)

- Recommendation: give hints how to store the cosmeto-textile, in order to have a guideline for “the usual storing conditions”.

5.1.5. Labeling With Warnings In Case of Health Risks

Intention: avoidance of health risks, allergies etc. In case there is an abstract possibility that the cosmetic product could cause any health irritations, a warning note is necessary. The general know application hints are not necessary (“do not eat”…), but there is a hint necessary, if the possibility can not be excluded, that a certain ingredient could lead to skin reactions (“Please do not wear the textile any longer in case of skin reactions”). The person, who places the cosmetic product on the market to the end consumer has to comply with the label requirement, which means brand owner.

5.1.6. Identification With The Batch Number

- Intention: to identify/ determ defective batches; to facilitate potential recalls; to facilitate the chemical analysis and to determine the reason for the defect
- The required data: date of manufacturing and content of the cosmetic product has to be traceable
- The person who is responsible for labeling: everybody, who packs the cosmetic product (in our case; textiles) and places it on the market to the end consumer
- In consequence: in case the cosmetic product is sold in bulks (unpacked) to the brand owner or its toll manufacturer, it is the brand owner’s obligation to comply with the label requirements

5.1.7. Identification With Labeling

- Intention: avoid misuse of cosmetic product (no eating, drinking etc.)
- The required data: the function of the cosmetic product has to be recognizable by the marketing campaign, the layout of hang tags, leporellos etc. If such function cannot be detected by the circumstances, the function has to expressively written on the label
- The person who is responsible for labeling: obligation to comply with such label requirement: again the brand owner being responsible for its own marketing campaign.

5.1.8. List of Ingredients

The necessary point:

- List shall be preceded by the word “ingredient”;
- Ingredients have to be listed in descending order of weight at the time they are added. (INCI-names are to be used)
- Ingredients in concentrations of less than 1 % may be listed in any order after those in concentration of more than 1 %.
- Coloring agents used shall be listed in any order, containing the word “may contain”.
- Perfume and aromatic compositions shall be referred to by the word “perfume” or “flavour”.
- Impurities, auxiliary substances, thinners, resolvers etc. which are only technically required to produce the cosmetic product, are no ingredients according to this provision.

5.1.9. The Right Place For Labeling

Law requires the labeling of “container” and “package”. Can jeans be regarded as a container or a package of cosmetic products?

Definition: “Container”: all packages that have certain form and keep this form (pots, glasses, boxes etc.)

Definition: “Packaging”: the overall amount of materials that serve to pack the cosmetic product (the plastic cover surrounding the pot)

Cosmeto Textile is considered as being the “container”, the “carrier” for the cosmetic products. But still under legal discussion that the current legal requirements are difficult to apply for cosmeto-textiles.

5.1.10. Identification With The Batch Number

Due to the containing cosmetic products, cosmeto-textiles have to comply with the following legal requirements:

- Label requirements according to Cosmetic Directive
- Publicity/ promotion for cosmetic products and cosmeto-textiles must not be misleading (the claims for the cosmeto-textile itself have to be based on evidenced tests)

- The overall impression for cosmetic products must not lead to the impression of presenting a pharmaceutical.
- The claimed features must not be hollowed promises. This leads to indemnification claims.

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